- **HYDROCARBON**
- **AROMATIC COMPOUND**
- **ALCOHOL AND ETHER**

Corporate Head Office

394 - Rajeev Gandhi Nagar Kota, (Raj.)

Ph. No. : 08003899588, 0744-2209671

IVRS No : 0744-2439051, 52, 53,

www. motioniitjee.com , info@motioniitjee.com

MOTION
Nurturing potential through education

CHEMISTRY

TARGET (JEE MAIN + JEE ADVANCED)

THEORY AND EXERCISE BOOKLET

CONTENTS

JEE SYLLABUS

- **HYDROCARBON**

JEE - ADVANCED

Preparation, properties and reactions of alkanes: Homologous series, physical properties of alkanes (melting points, boiling points and density); Combustion and halogenation of alkanes; Preparation of alkanes by Wurtz reaction and decarboxylation reactions.
Preparation, properties and reactions of alkenes and alkynes: Physical properties of alkenes and alkynes (boiling points, density and dipole moments); Acidity of alkynes; Acid catalysed hydration of alkenes and alkynes (excluding the stereochemistry of addition and elimination); Reactions of alkenes with $KMnO_4$ and ozone; Reduction of alkenes and alkynes; Preparation of alkenes and alkynes by elimination reactions; Electrophilic addition reactions of alkenes with X_2, HX, HOX (X=halogen) and H_2O; Addition reactions of alkynes; Metal acetylides.

- **AROMATIC COMPOUND**

JEE - ADVANCED

Reactions of benzene: Structure and aromaticity; Electrophilic substitution reactions: halogenation, nitration, sulphonation, Friedel-Crafts alkylation and acylation; Effect of o-, m- and p-directing groups in monosubstituted benzenes. Phenols: Acidity, electrophilic substitution reactions (halogenation, nitration and sulphonation); Reimer-Tieman reaction, Kolbe reaction. basicity of substituted anilines, preparation from nitro compounds, reaction with nitrous acid, azo coupling reaction of diazonium salts of aromatic amines, Sandmeyer and related reactions of diazonium salts; carbylamine reaction; Haloarenes: nucleophilic aromatic substitution in haloarenes and substituted haloarenes (excluding Benzyne mechanism and Cine substitution).

- **ALCOHOL AND ETHER**

JEE - ADVANCED

Alcohols: esterification, dehydration and oxidation, reaction with sodium, phosphorus halides, ZnCl2/concentrated HCl, conversion of alcohols into aldehydes and ketones; Ethers:Preparation by Williamson's Synthesis;

ALKANE

Alkane are the saturated non polar hydrocarbon having general formula C_nH_{2n+2}.

Hydrocarbon – Those organic compounds which contain only carbon and hydrogen atoms are known as hydrocarbons.

1.2 General method of preparation

1.2.1 By catalytic reduction of alkenes and alkynes

$$R - C \equiv C - R' \xrightarrow[Ni,Pt \text{ or } Pd]{H_2,25^oC} R - CH_2 - CH_2 - R'$$

$$R - CH = CH - R' \xrightarrow[Ni,Pt \text{ or } Pd]{H_2,25^oC} R - CH_2 - CH_2 - R'$$

Hydrogenation $\rightarrow$ Addition of H_2 to unsaturated bond.

Hydrogenation is of two kind

(a) Heterogeneous and (b) Homogeneous

(a) Heterogeneous $\rightarrow$ It is two phase hydrogenation the catalyst is finely divided metal like Ni, Pt or Pd and a solution of alkene.

(b) Homogeneous $\rightarrow$ It is one phase hydrogenation both catalyst and alkenes are solution. In this hydrogenation catalyst are organic complex of transition metal like Rh or Ir.

Hydrogenation is exothermic, qualitative and during the hydrogenation, total heat evolved to hydrogenate one mole of unsaturated compound is called heat of hydrogenation. Heat of hydrogenation is the measurement of stability of isomeric alkenes.

$$\text{stability of alkene} \propto \frac{1}{\text{Heat of hydrogenation}}$$

1.2.2 From alkyl halide

(A) From organometallic compound $\rightarrow$ compound having $\overset{\delta-}{C} - \overset{+\delta}{M}$ bond. (M $\rightarrow$ metal)

(i) By wurtz reaction

$$2R - X + 2Na \xrightarrow{\text{dry ether}} R - R + 2NaX$$

$$R - X + R' - X \xrightarrow[\text{ether (dry)}]{Na} R - R,\ R - R',\ R' - R'$$

Mechanism $\longrightarrow$ Two mechanisms are suggested

(a) Ionic mechanism

$2Na \longrightarrow 2Na^{\oplus} + 2e^{\ominus}$

$R - X + 2e^- \longrightarrow \overset{\ominus}{R} + \overset{\ominus}{X}$

(1º, 2º)

$\overset{\ominus}{R} + R - X \xrightarrow{SN^2} R - R$

(1º or 2º)

$\overset{\ominus}{Na} + \overset{\oplus}{X} \longrightarrow NaX$

(b) Free radical mechanism

$Na \longrightarrow \overset{\oplus}{Na} + \overset{\ominus}{e}$

$R - X + \overset{\ominus}{e} \longrightarrow R^{\bullet} + X^{\ominus}$

$R^{\bullet} + R^{\bullet} \longrightarrow R-R$

Note : The alkyl halide should be 1º or 2º, with 3º R – X SN^2 and free radical coupling is not possible due to steric hinderance so in that case elimination or disproportionation is possible.

In the ionic mechanism alkyl sodium ($\overset{\ominus}{R}\ \overset{\oplus}{Na}$) gives $\overset{\ominus}{R}$ strong base as well as nucleophile which gives SN^2 with R – X, ether should be dry otherwise, if moisture is present then $\overset{\ominus}{R}$ forms R – H instead of R – R with H_2O.

(ii) By G.R. $\underset{1^o,2^o,3^o}{R-X} \xrightarrow[ether]{Mg} RMgX$

$RMgX + \underset{\text{compound}}{\text{all active H containg}} \longrightarrow R - H$

$RMgX \xrightarrow{H_2O} R - H + Mg(OH)X$

$RMgX \xrightarrow{ROH} R - H + Mg(OR)X$

$RMgX \xrightarrow{NH_3} R - H + Mg(NH_2)X$

$RMgX \xrightarrow{R' - C \equiv CH} R - H + Mg\,C \equiv CR')$

$RMgX \xrightarrow{RSH} R - H + Mg(SR)X$

$RMgX \xrightarrow{R - COOH} R - H + Mg(OCOR)X$

(iii) By corey house alkane synthesis

$\underset{(1^o,2^o,3^o)}{R-X} \xrightarrow{2Li} \overset{\ominus}{R}\ \overset{\oplus}{Li} + LiX \xrightarrow{CuX} \underset{\text{Lithium dialkyl cuprate (Gilman Reagent)}}{R_2CuLi} \xrightarrow[(1^o > 2^o)]{R' - X} R - R'$

Mechanism

R_2CuLi is the source of $^{\ominus}R$

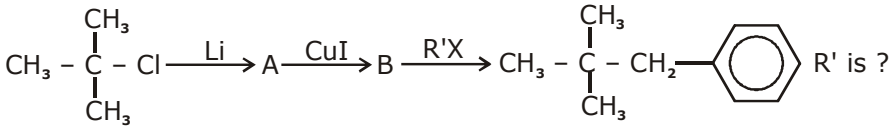
$\overset{\ominus}{R} + \underset{1^o >> 2^o}{R' - X} \xrightarrow{SN^2} R - R'$

R_2 CuLi do not reacts with $-NO_2$, – CN, > C = O etc.

Ex.1 $CH_3 - Br \xrightarrow{Li} A \xrightarrow{CuI} B \xrightarrow{Y} C$

if C is $CH_3 - CH_2 - (CH_2)_5 - CH_3$, than what is Y.

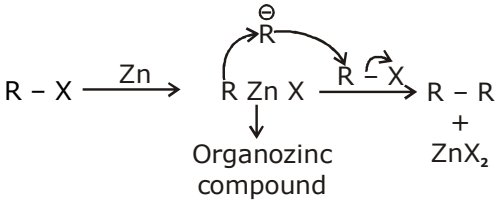
Ans. $CH_3 - (CH_2)_6 - Br$

Q.1 

(iv) By Franklande reagent

$R - X + Zn + R - X \xrightarrow{Ether} R - R + Zn X_2$

Mechanism



(B) By reduction of alkyl halides

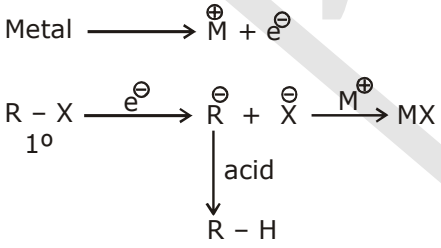
(i) with metal-acid

$$\underset{1^o}{R - X} \xrightarrow[\text{Metal / acid}]{e^{\ominus} / H^{\oplus}} R - H + HX$$

Reducing agent

Zn / acid, Zn – Cu / H_2O or Zn – Cu + acid
Zn – Cu / C_2H_5OH, Na – Hg / acid, Al – Hg / H_2O etc.

Mechanism



(ii) With Metal hydrides

(a) TPH (Ph_3SnH) : It reduces 1°, 2° & 3° R – X

$R - X \xrightarrow{Ph_3SnH} R - H$

(b) $NaBH_4$ $\underset{1^o \& 2^o}{R - X} \xrightarrow{NaBH_4} R - X$

(c) $\underset{1^o \& 2^o}{R - X} \xrightarrow{LiAlH_4} R - H$, $\underset{3^o}{R - X} \xrightarrow{LiAlH_4}$ Alkene

1.2.3 By red P & HI

Red P & HI is strong reducing agent

$$R - COOH \xrightarrow{\text{Red P + HI}} R - CH_3$$

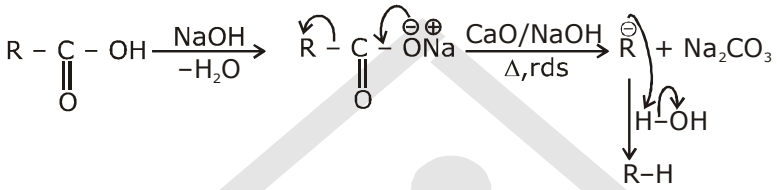
$$R - \underset{\underset{O}{\|}}{C} - Cl \xrightarrow{\text{Red P + HI}} R - CH_3$$

$$R - \underset{\underset{O}{\|}}{C} - OEt \xrightarrow{\text{Red P + HI}} R - CH_3$$

$$R - X \xrightarrow{\text{Red P + HI}} R - H$$

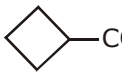
$$R - OH \xrightarrow{\text{Red P + HI}} R - H + H_2O$$

1.2.4 By soda lime $\rightarrow$ Fatty acids are good source of hydrocarbon, correction, heating of sodium salt of carboxylic acid (R – COONa) with soda lime (NaOH – CaO) gives hydrocarbon, which is known as decarboxylation (e.g. replacement of – COOH group by –H) decarboxylation also takes place on heating only, when compound is gem dicarboxylic acid or there is keto group or double bond on β carbon.

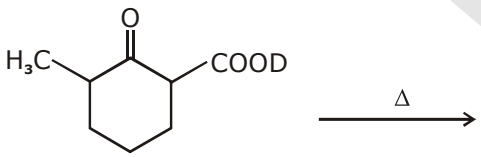


Ex.2 

What are A and B

Ans. A is 

, B is 

Q.2 

Optically active

Write the structure of A and mention its stereochemistry

1.2.5 **By Kolbe's electrolysis**

$$2RCOOK + 2HOH \xrightarrow{\text{Electrolysis}} RR + 2CO_2 + H_2 + 2KOH$$

e.g. $2CH_3 - COOK + 2H_2O \xrightarrow{\text{Electrolysis}} CH_3CH_3 + 2CO_2 + H_2 + 2KOH.$

If n is the number of carbon atoms in the salt of carboxylic acid, the alkane formed has 2(n – 1) carbon atoms.

1.2.6 **Reduction of aldehydes, ketones :**

(a) By Clemmensen's reduction : with Zn – Hg / conc. HCl

$$R - CHO \xrightarrow[\Delta]{Zn - Hg\ /conc.\ HCl} RCH_3 + H_2O$$

$$R - \overset{\overset{O}{\|}}{C} - R' \xrightarrow[\Delta]{Zn - Hg\ /conc.\ HCl} RCH_2R' + H_2O$$

e.g. $CH_3 - CHO \xrightarrow[\Delta]{Zn - Hg\ /conc.\ HCl} CH_3CH_3 + H_2O$

$$CH_3 - \overset{\overset{O}{\|}}{C} - C_2H_5 + 4[H] \xrightarrow[\Delta]{Zn - Hg\ /conc.\ HCl} CH_3CH_2C_2H_5 + H_2O$$

Clemmensen reduction is not used for compound which have acid sensitive group.

(b) By Wolff-kishner reduction with NH_2NH_2 / KOH

$$RCHO \xrightarrow[\Delta]{NH_2NH_2\ /\ KOH} RCH_3$$

$$RCO - R' \xrightarrow[\Delta]{NH_2NH_2\ /\ KOH} RCH_2R'$$

Wolff-kishner reduction is not used for compounds which have base sensitive groups.

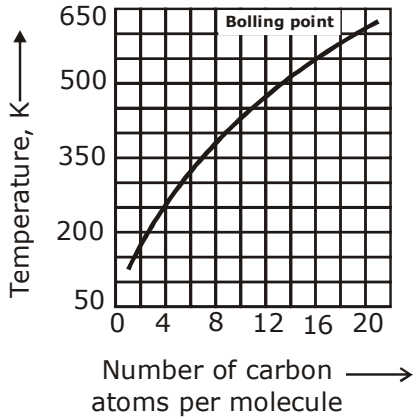
1.3 Physical Properties of Alkanes :

3.3.1 Physical State :

The first four members (C_1 to C_4) are gases : the next thirteen members, (C_5 to C_{17}) are liquids while the higher members are waxy solids.

1.3.2 **Boiling points :**

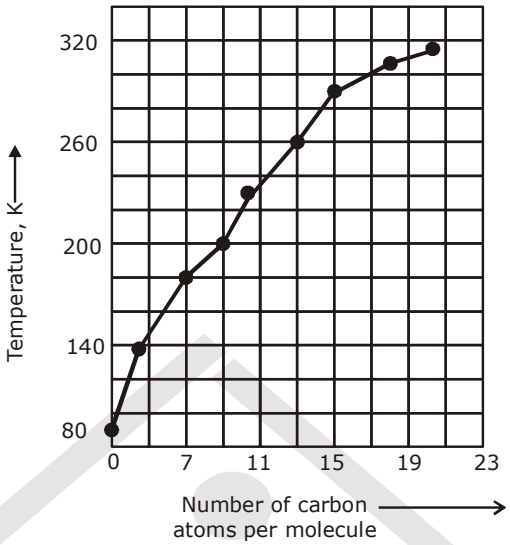
The boiling points of n-alkanes increase regularly with the increase in the number of carbon atoms



Among the isomeric alkanes, the branched chain isomers have relatively low boiling points as compared to their corresponding straight chain isomers. Greater the branching of the chain, lower is the boiling point. This is due to the fact that branching of the chain makes the molecules more compact and brings it close to a sphere, so the magnitude of vander wall forces decreases.

1.3.3. Melting Points

It is the evident that the increase in melting point is relatively more in moving from an alkane having odd number of carbon atoms to the higher alkane with even no. of 'C' while it is relatively less in moving from an alkane with even number of carbon atoms to the higher alkane.
Explanation : The alkanes with even no. of 'C' atoms are more closely packed.



1.3.4 Solubility

In keeping with the popular rule "like dissolves like" hydrocarbons are insoluble in polar solvent like water because they are predominantly non-polar in nature.

1.3.5 Density

The densities of alkanes increase with increasing molecular weight but become constant at about 0.8 g cm^{-3}. This means that all alkanes are lighter than water so they floats over water.

1.4.1 Chemical Reaction of Alkanes :

Characteristic reaction of alkanes are free radical substitution reaction, these reaction are generally chain reactions which are completed in three steps mainely.
(i) chain initiation (ii) chain propagation, (iii) chain termination

Examples of free radical substitution reaction $\rightarrow$

$$R - H + X_2 \xrightarrow[250^o - 400^oC]{\text{UV Light or}} R - X + HX$$

Exp.
$$CH_4 \xrightarrow[h\nu]{Cl_2} \underset{+\ HCl}{CH_3Cl} \xrightarrow[h\nu]{Cl_2} \underset{+\ HCl}{CH_2Cl_2} \xrightarrow[h\nu]{Cl_2} \underset{+\ HCl}{CHCl_3} \xrightarrow[h\nu]{Cl_2} CCl_4$$

When equimolar amount of methane and Cl_2 are taken, a mixture of four possible products are formed,

but if we take excess of CH_4 then yield of CH_3Cl will be the major product.

Reactivity of X_2 : $F_2 > Cl_2 > Br_2 > I_2$

Reactivity of H : $3^oH > 2^oH > 1^oH$

with F_2 alkanes reacts so vigorously that, even in the dark and at room temp, reactant diluted with an inert gas.

Iodination is reversible reaction, since HI formed as a by-product is a strong reducing agent and reduces alkyl iodide back to alkane. Hence iodination can be done only in presence of strong oxidizing agent like HIO_3, HNO_3 or HgO

$$R - H + I_2 \rightleftharpoons R - I + HI$$

$$HI + HIO_3 \longrightarrow H_2O + I_2$$

Mechanism of halogenation of CH_4 $\longrightarrow$

(i) Chain initiation $\rightarrow$ it is a endothermic step

$$X_2 \xrightarrow[250^o - 400^oC]{\text{UV or temp}} 2\overset{\bullet}{X}$$

(ii) Chain propagation $\rightarrow$

$$\overset{\bullet}{X} + R - H \longrightarrow \overset{\bullet}{R} + HX$$

$$\overset{\bullet}{R} + X - X \longrightarrow R - X + \overset{\bullet}{X}$$

(iii) Chain termination $\rightarrow$ it is always exothermic

$$\overset{\bullet}{X} + \overset{\bullet}{X} \longrightarrow X_2$$

$$\overset{\bullet}{R} + \overset{\bullet}{R} \longrightarrow R - R$$

$$\overset{\bullet}{R} + \overset{\bullet}{X} \longrightarrow R - X$$

Each photon of light cleaves one chlorine molecule to form two chlorine redicals, each chlorine atom starts a chain and on an average each chain contains 5000 repetitions of the chain propagating cycle so about 10,000 molecules of CH_3Cl are formed by one photon of light.

Some reagent affects the rate of halogenation : For example

Q.3 In the given ways which is feasible

$$CH_4 + \overset{\bullet}{Cl} \begin{cases} \longrightarrow \overset{\bullet}{C}H_3 + HCl \longrightarrow (1) \\ \longrightarrow CH_3Cl + \overset{\bullet}{H} \longrightarrow (2) \end{cases}$$

Q.4 Which of the following reaction has zero activation energy

(A) $CH_4 + \overset{\bullet}{Cl} \longrightarrow \overset{\bullet}{C}H_3 + HCl$ (B) $Cl_2 \longrightarrow 2\,Cl$

(C) $\overset{\bullet}{C}H_3 + \overset{\bullet}{C}H_3 \longrightarrow CH_3 + CH_3$ (D) $\overset{\bullet}{C}H_3 + Cl - Cl \longrightarrow CH_3 + Cl + \overset{\bullet}{Cl}$

Q.5 If the E_{act} for a forward reaction is given

$CH_3 - H + \dot{Cl} \longrightarrow \dot{C}H_3 + HCl$ $\quad \Delta H = +1$ kcal, $E_{act} = 4$ kcal

the E_{act} for backward reaction will be

(A) 1 kcal (B) 4 kcal (C) –4 kcal (D) 3 kcal

Halogenations of higher alkane :

(i) $CH_3 - CH_2 - CH_3 \xrightarrow[\text{light, } 25^oC]{Cl_2} \underset{55\%}{CH_3 - \underset{Cl}{CH} - CH_3} + \underset{45\%}{CH_3 - CH_2 - CH_2 - Cl}$

(ii) $CH_3 - CH_2 - CH_2 - CH_3 \xrightarrow[\text{light, } 25^oC]{Cl_2} \underset{72\%}{CH_3 - CH_2 - \underset{Cl}{CH} - CH_3} + \underset{28\%}{CH_3 - CH_2 - CH_2 - CH_2 - Cl}$

(iii) $CH_3 - \underset{CH_3}{CH} - CH_3 \xrightarrow[\text{light, } 25^oC]{Cl_2} \underset{64\%}{CH_3 - \underset{CH_3}{CH} - CH_2 - Cl} + \underset{36\%}{CH_3 - \underset{Cl}{\overset{CH_3}{C}} - CH_3}$

(iv) $CH_3 - CH_2 - CH_3 \xrightarrow[\text{light, } 127^oC]{Br_2} \underset{3\%}{CH_3 - CH_2 - CH_2 - Br} + \underset{97\%}{CH_3 - \underset{Br}{CH} - CH_3}$

(v) $CH_3 - \underset{CH_3}{CH} - CH_3 \xrightarrow[\text{light, } 127^oC]{Br_2} \underset{\text{trace}}{CH_3 - \underset{CH_3}{CH} - CH_2Br} + \underset{\text{over } 99\%}{CH_3 - \underset{CH_3}{\overset{CH_3}{C}} - Br}$

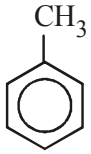
Relative amounts of the various isomers differ remarkably depending upon the halogen used from the above reaction, it is observed that chlorination gives mixture in which no isomer greatly dominates while, in bromination gives mixture in which one isomer dominates greatly (97% – 99%).

Factors determining the relative yields of the isomeric products.

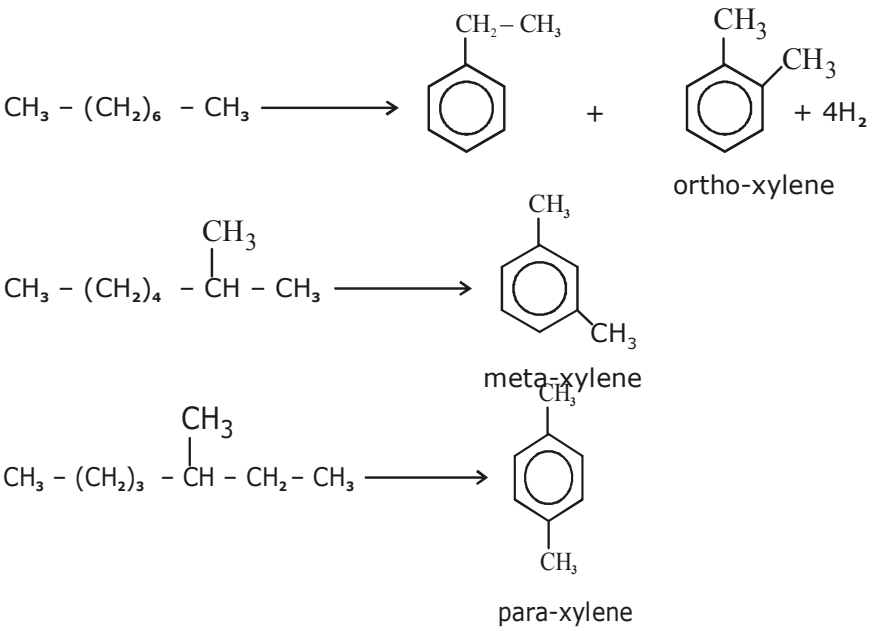
(i) Probability factor $\rightarrow$ This factor is based on the number of each kind of H atom in the molecule.

(ii) Reactivity of hydrogen $\rightarrow$ The order of reactivity is $3^o > 2^o > 1^o$

1.4.2 Aromatisation:

$CH_3 - (CH_2)_5 - CH_3 \xrightarrow[600^oC]{CrO_3 + Al_2O_5}$  $+ 4H_2$

Toluene



1.4.3 Combustion : (i.e. complete oxidation)

$$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right) O_2 \xrightarrow[\Delta]{\text{combustion}} nCO_2 + (n+1)\,H_2O \ (\Delta H_{combustion} = -ve)$$

$$C_xH_y + \left(x + \frac{y}{4}\right) O_2 \xrightarrow[\Delta]{\text{combustion}} xCO_2 + \frac{y}{2}\,H_2O$$

$$C_5H_{12} + 8O_2 \xrightarrow[\Delta]{\text{combustion}} 5CO_2 + 6H_2O$$

Heat of combustion : Amount of heat i.e. liberated when 1 mole of hydrocarbon is completely burnt into CO_2 & H_2O.

Heat of combustion as a measure of stability of alkane :
Combustion is used as a measurements of stability.
More branched alkanes are more stable and have lower heat of combustion.

e.g. (I) $CH_3 - CH_2 - CH_2 - CH_3$ (II) $CH_3 - \underset{\displaystyle H}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}} - CH_3$

stability : II > I
$\Delta H_{comb.}$: I > II

More branched alkane has more no. of primary C – H bonds. (therefore it has more bond energy).
Homologues : Higher homologues have higher heat of combustion.
Isomers : Branched isomer has lower heat of combustion.

(i) Initiators → they initiate the chain reaction, initiators are R_2O_2, Perester's etc.

$$R - O - O - R \xrightarrow[\text{temp}]{\text{hv or}} R\,\dot{O}$$

$$R - \underset{\displaystyle O}{\overset{\displaystyle \|}{C}} - O - O - \underset{\displaystyle O}{\overset{\displaystyle \|}{C}} - R \xrightarrow[\text{temp}]{\text{hv or}} R - C - \dot{O}$$

(ii) Inhibitors → A substance that slow down or stop the reaction are known as inhibitors
For example O_2 is a good inhibitor

$$\dot{R} + O_2 \longrightarrow R - O - \dot{O} + \dot{R} \longrightarrow R - O - O - R$$

all reactive alkyl free radicals are consumed so reaction become stop for a period of time.

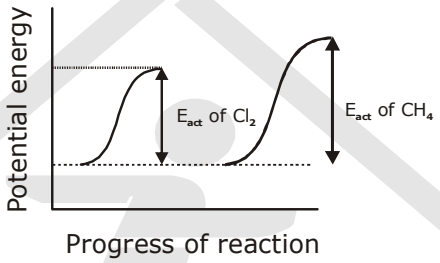
Relative reactivity of halogen toward methane ⟶
Order of reactivity is $F_2 > Cl_2 > Br_2 > I_2$ which can be explained by the value of ΔH (energy change)

Steps of halogenation, value of ΔH for each step. (Kcal/mole)

	F	Cl	Br	I
(i) $X_2 \longrightarrow 2X$		+ 38	+ 58	+ 46 + 38
(ii) $\dot{X} + CH_4 \longrightarrow \dot{C}H_3 + HX$		–32	+ 1	+ 16 + 33
(iii) $\dot{C}H_3 + X \longrightarrow CH_3X + \dot{X}$		– 70	– 26	– 24 – 20

Ex.3 Explain why the chain initiating step in thermal chlorination of CH_4 is
$Cl_2 \xrightarrow{\Delta} \dot{Cl}$ and not $CH_4 \xrightarrow{\Delta} \dot{C}H_3 + \dot{H}$

Ans. Because E_{act} of Cl_2 is less than E_{act} of CH_4



Ex.4 Chlorination of CH_4 involves following steps :

(i) $Cl_2 \longrightarrow 2\dot{Cl}$

(ii) $CH_4 + \dot{Cl} \longrightarrow \dot{C}H_3 + HCl$

(iii) $\dot{C}H_3 + \dot{Cl} \longrightarrow CH_3Cl$

Which of the following is rate determining ?
(A) Step (i)
(B) Step (ii)
(C) Step (iii)
(D) Step (ii) and (iii) both

Ans. (B)
Reactivity of hydrogen → 3º > 2º > 1º
Because formation of alkyl free radical is Rds so, that H is more reactive which produce more stable free radical (less E_{act})

order of stability of F.R. →

$$Ph_3\dot{C} > Ph_2\dot{C}H > Ph - \dot{C}H_2 > CH_2 = CH - \dot{C}H_2 > 3^o > 2^o > 1^o > \dot{C}H_3$$

ALKENE

1. INTRODUCTION

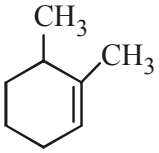
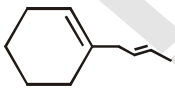
Alkenes are hydrocarbons with carbon–carbon double bonds, Alkenes are sometimes called olefins, a term derived from olefinic gas, meaning "oil forming gas". Alkenes are among the most important industrial compound and many alkenes are also found in plants and animals. Ethylene is the largest – volume industrial organic compound, used to make polyethylene and a variety of other industrial and consumer chemicals.

2. Structure and bonding in Alkenes

(1) Alkenes are unsaturated hydrocarbons having at least one double bond.
(2) They are represented by general Formula (G.F.) C_nH_{2n} (one double bond)
(3) In Ethene C = C bond length is 1.34 Å
(4) Its bond energy is 146 kcal.mol^{-1}
(5) The hybridization of (C = C) alkenic carbon is sp^2
(6) The πe^- cloud is present above and below the plane of σ–bonded skeleton.
(7) They are also known as olefins since ethene, the first member of the homologous series forms oily liquid substance when treated with halogens.
(8) Compounds may exist as conjugated polyenes or as cumulated polyenes or as isolated polyenes

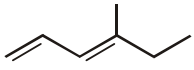
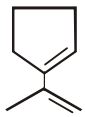
Note : That angle a > b since repulsion due to π electrons (double bond - single bond repulsion > single bond single bond repulsion according to VSEPR theory.

Ex.1 Write IUPAC names of

(a)  (b) 

Ans. (a) 2, 3-Dimethylcyclohexene
(b) 1-(2-butenyl) cyclohex –1–ene

Ex.2 Give the structure for each of the following
(a) 4-Methyl-1, 3-hexadiene
(b) 1-Isopropenylcyclopentene

Ans. (a)  (b) 

3. Physical Properties of Alkenes / Hydrocarbons

Table : III

	Physical properties	Homologus series	Isomers
1.	Physical state	$C_1 - C_3$ gases $C_4 - C_{20}$ liquids $>C_{20}$: solids	
2.	Dipolemoment (μ)		cis > trans
3.	Polarity	–	cis > trans (for $C_{ab} = C_{ab}$ type of alkenes
4.	Melting point	increases with M.W.	trans > cis (due to more packing capacity)
5.	Boiling point	increases with M.W.	cis > trans # branching decreases B.P. C C – C = C < C – C = C – C Polarity increases, boiling point increases
6.	Solubility	Practically insoluble in water but fairly soluble in nonpolar solvents like benzene petroleum ether, etc.	cis > trans Polarity increases, solubility in polar solvents increases.
7.	Stability		trans > cis (cis isomers has more Vander Waals repulsion)

4. Laboratory test of Alkene

Table - IV

Functional Group	Reagent	Observation	Reaction	Remarks
C = C	(1) Bayer's Reagent alk. dil. Cold $KMnO_4$	Pink Colour disappears	$CH_2 = CH_2 + H_2O + O \xrightarrow{\text{alk. } KMnO_4} CH_2(OH) - CH_2(OH)$	Dihydroxylation
	(2) Br_2 / H_2O	Bromine water Colour decolourises	$Br_2 + CH_2 = CH_2 \longrightarrow CH_2(Br) - CH_2(Br)$ White ppt	Dibromination
	(3) O_3 (ozone)	C = O Compounds	$H_2C = CH_2 + O_3 \xrightarrow{Zn / H_2O} 2HCHO$	Ozonolysis

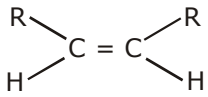
5. Methods of preparation of alkenes

(I) BY PARTIAL REDUCTION OF ALKYNES

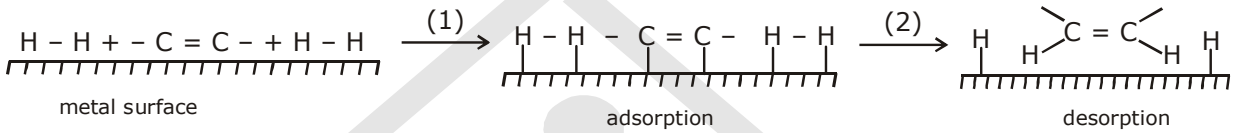
(a) By Catalytic Hydrogenation of Alkynes in presence of poisoned catalyst (A Syn Addition of Hydrogen : Synthesis of cis-Alkenes : This is performed by)

(i) Lindlar's catalyst : Metallic palladium deposited on calcium carbonate with lead acetate and quinoline.

(ii) P-2 catalyst (Ni_2B nickel boride)

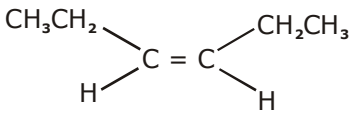
General Reaction $R - C \equiv C - R \xrightarrow[\text{quinoline}]{H_2Pd / CaCO_3 \text{ (Lindlar's catalyst)}}$ 

Mechanism of hydrogenation :



Steps : The reactant alkyne molecules and hydrogen molecules get adsorbed at the surface of metal catalyst. It is chemical adsorption (chemisorption).

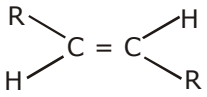
In this state, the reactants lie very close to each other and so the hydrogen atoms start forming bond with carbon. Two hydrogen atoms are added to two triply bonded carbon atom from the same side of π bond and a **cis or syn addition product** is formed. The product alkene now escapes away from the surface of the catalyst. Quinoline occupies the metal surface inhibiting further reduction to alkanes **Quinoline** therefore is called **catalyst poison** and palladium is called deactivated catalyst or poisoned catalyst.

e.g. $CH_3CH_2C = CCH_2CH_3 \xrightarrow[\text{(syn addition)}]{H_2/Ni_2B(P\text{-}_2) \text{ or } H_2/Pd/CaCO_3}$ 

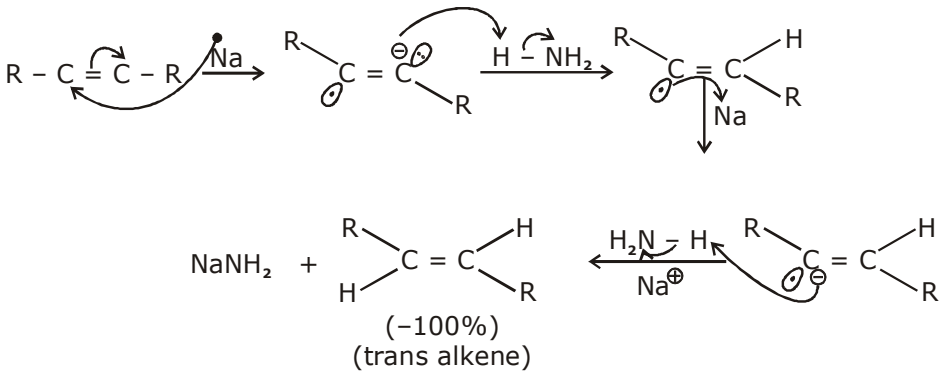
3-Hexyne

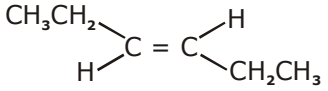
(Z)-3-Hexene
(cis-3-hexene)
(97%)

(b) Birch Reduction : (Anti Addition of Hydrogen : Synthesis of trans-Alkenes)

General Reaction $R - C \equiv C - R \xrightarrow[\text{Liq. } NH_3]{Na / Li}$ 

Mechanism : Reagents Na(or Li, K) + liq $NH_3 \longrightarrow Na^+ + e^-$ (solvated electron)



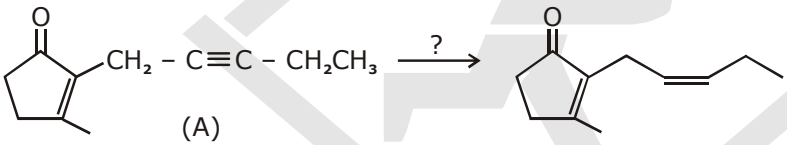
e.g. $CH_3 - CH_2 - C = C - CH_2 - CH_3 \xrightarrow{Na / NH_3 (l)}$ 

trans
hex-3-ene

Note : This process of reduction is not eligible when terminal alkynes are taken. ($R - C \equiv CH$) because terminal alkynes form sodium salt with Na metal.

$CH_3 - C = CH + Na / NH_3 \longrightarrow CH_3 - CH = C - Na^+ + [H]^+$

Ex.3 Identify the reagent for following synthesis.

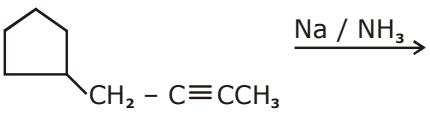


(A) cis Jasmone

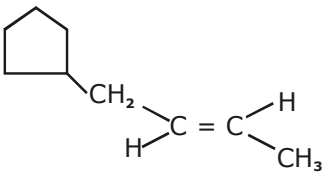
Ans. H_2 / Lindiar's catalyst.

A $\xrightarrow[\text{Lindlar's catalyst}]{H_2}$ cis - Jasmone

Ex.4 Identify the products in the following reaction :



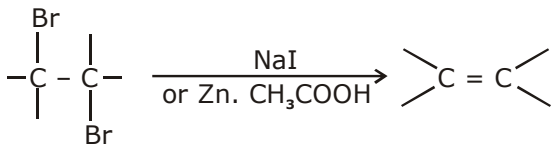
Ans.

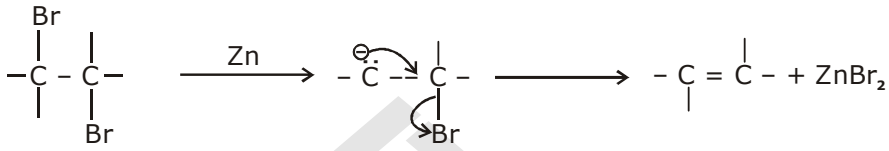


(II) BY DEHAL OGENATION OF VICINAL DIHALIDES

There are two types of dihalides namely gem (or geminal) dihalides in which the two halogen atoms are attached to the same carbon atom and vicinal dihalides in which the two halogen atoms are attached to the adjacent carbon atoms.
Dehalogenation of vicinal dihalides can be effect either by NaI in acetone or zinc in presence of acetic acid or ethanol.

General Reaction

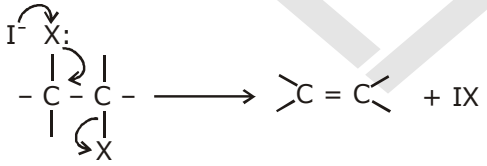
(i) 

Mech. 

(ii) $CH_3 - CHBr - CH_2Br \xrightarrow[\left(\begin{array}{l}CH_3COOH \text{ or}\\ C_2H_5OH \text{ as solvent}\end{array}\right)]{\text{Zn dust}} CH_3 - CH = CH_2$

Mech.

With NaI in acetone :



It involves an **antielimination** of halogen atoms

Remarks
(1) Both are E2 elimination.
(2) Both are stereospecific anti elimination.

(III) DEHYDRO HALOGENATION OF ALKYL HALIDES

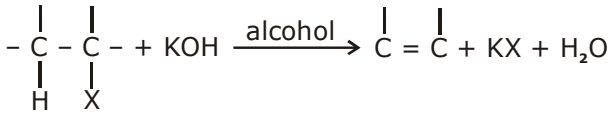
Dehydro halogenation is the elimination of a hydrogen and a halogen from an alkyl halide to form an alkene.

Dehydro halogenation can take place by E1 and E2 mechanism.

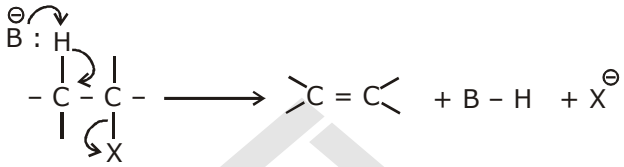
(i) Hot alcoholic solution of KOH EtO^- / EtOH (ii) $NaNH_2$
(iii) t-BuO–K^+ in t-BuOH

(i) Dehydrohalogenation by the E2 mechanism : Second-order elimination is a reliable synthetic reaction, especially if the alkyl halide is a poor S_N2 substrate. E2 dehydrohalogenation takes place in one step, in which a strong base abstracts a proton from one carbon atoms as the leaving group leaves the adjacent carbon.

General reaction :



Mechanism

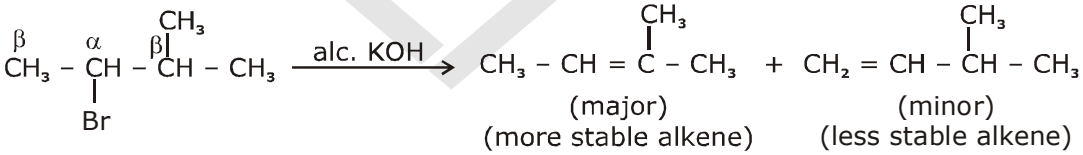


Undergo elimination of hydrogen halide (HX) leading to the formation of alkenes.

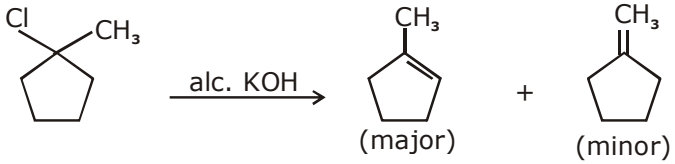
e.g.

Here β – H is eliminated by base hence called **β elimination** following **Saytzeff rule.**
i.e, (Highly substituted alkene is major product). It also involves an anti elimination of HX.

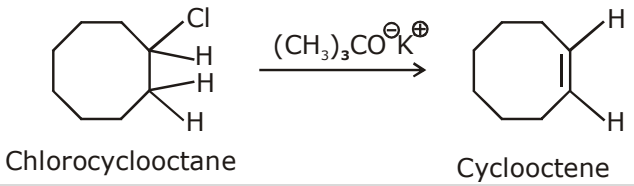
e.g.



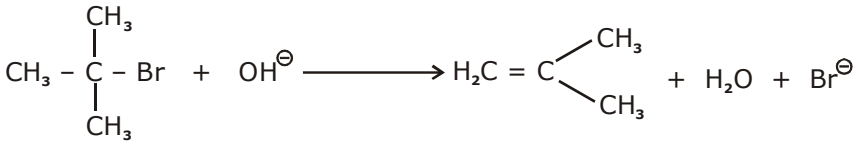
e.g.



e.g.

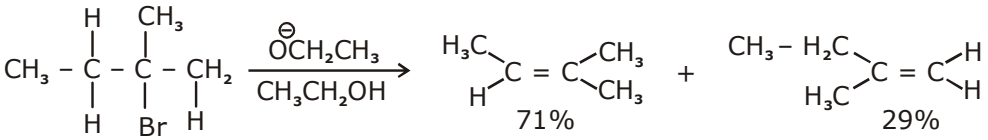


e.g.



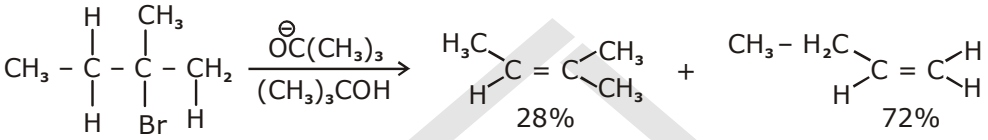
(ii) Formation of the Hoffmann product

Bulky bases can also accomplish dehydro halogenation that do not follow the saytzeff rule. Due to steric hindrance, a bulky base abstracts the proton that leads to the most highly substituted alkene. In these cases, it abstracts a less hindered proton, often the one that leads to formation of the least highly substituted product, called the Hoffmann product.



71%
Saytzeff product

29%



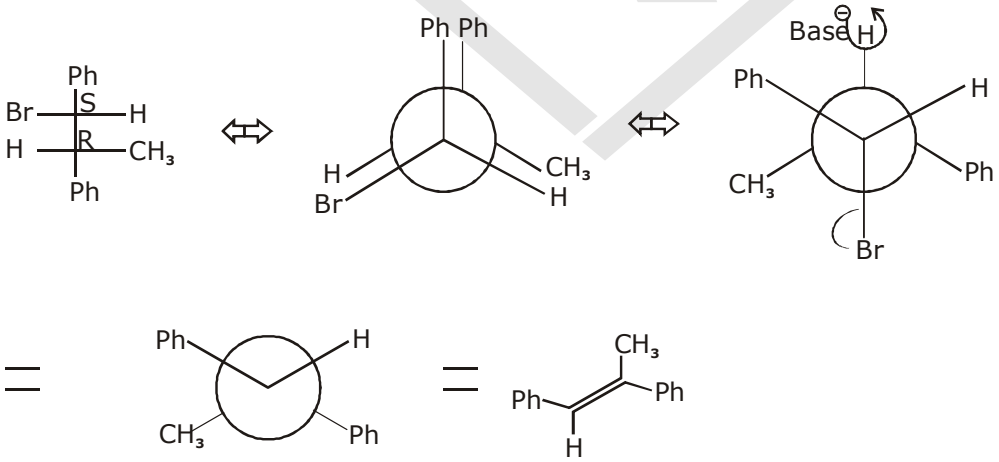
less hindered

28%

72%

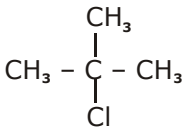
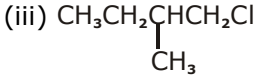
Stereospecific E2 reactions

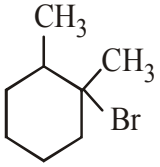
The E2 is stereospecific because it normally goes through an anti and coplanar transition state. The products are alkene, and different diastereomers of starting materials commonly give different diastereomers of alkenes.

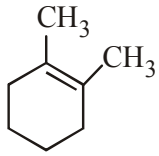
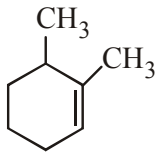
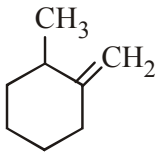


Ex.5 What alkyl halide would yield each of the following pure alkene on reaction with alcoholic KOH ?

(i) $CH_3 - \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}} = CH_2$ (ii) $CH_3 - CH_2 - CH_2 - CH = CH_2$ (iii) $CH_3 - CH_2 - \underset{\displaystyle CH_3}{\overset{\displaystyle CH_2}{\overset{|}{\underset{|}{C}}}} = CH_2$

Ans. (i)  (ii) $CH_3CH_2CH_2CH_2CH_2Cl$ (iii) 

Ex.6 What are the various product due to loss of HBr from 

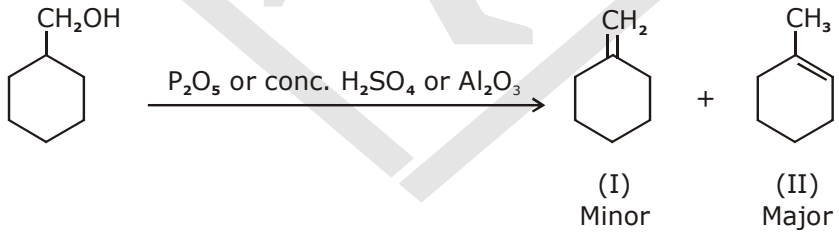
Ans.  (major)  (minor)  (minor)

(IV) DEHYDRATION OF ALCOHOLS

Alcohols when heated in presence of following reagents undergo loss of water molecule and form alkenes. The elimination is β **elimination.**

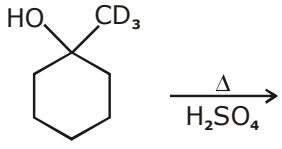
(i) H_2SO_4 / 160ºC
(ii) H_3PO_4 / Δ
(iii) P_2O_5 / Δ
(iv) Al_2O_3 / 350ºC undergo loss of water molecule and form alkenes

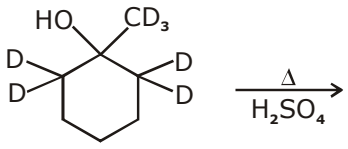
General Reaction $RCHCH_2OH \xrightarrow{P_2O_5 \text{ or conc. } H_2SO_4 \text{ or } Al_2O_3} R - CH = CH_2 + H_2O$

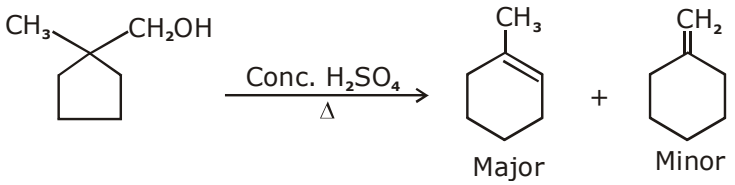
e.g. 

(I) Minor (II) Major

Q.1 If the starting material is labelled with deuterium as indicated, predict how many deuterium will be present in the major elimination product ?

(a) 

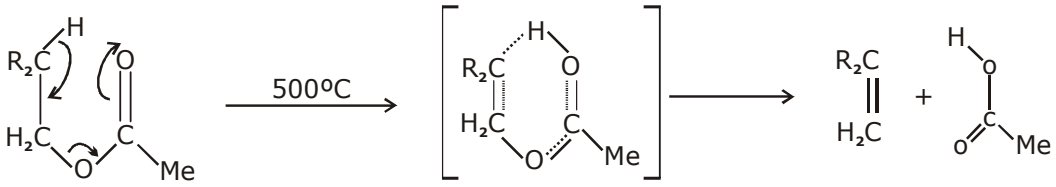
(b) 

Q.2 

Explain the mechanism ?

(V) BY PYROLYSIS OF ESTERS

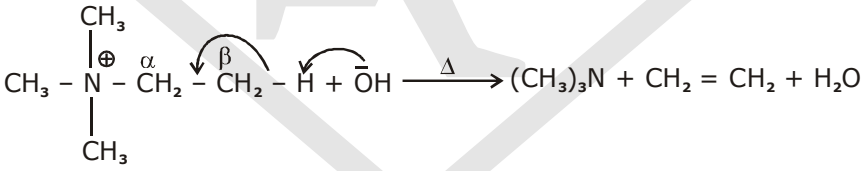
Thermal cleavage of an ester involves formations of a six membered ring in the transition state leading to the elimination of an acid leaving behind an alkene.

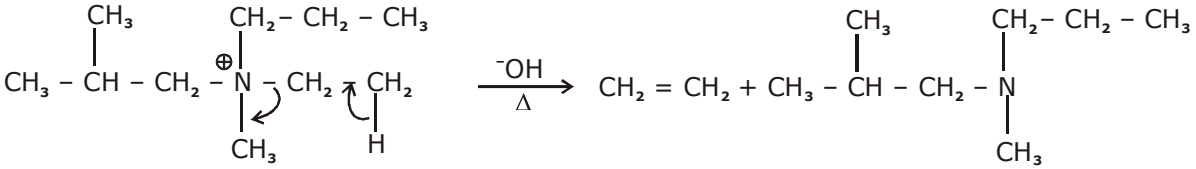


As a direct consequence of cyclic transition state, both the leaving groups namely proton and carboxylate ion are eliminated from the cis position. This is an example of **syn elimination.**

(VI) BY HOFMANN ELIMINATION METHOD

Alkenes can be prepared by heating quaternary ammonium hydroxide under reduced pressure at a temperature between 100ºC and 200ºC.
Less substituted alkenes are formed as major product in this case, which are defined as Hofmann alkenes.

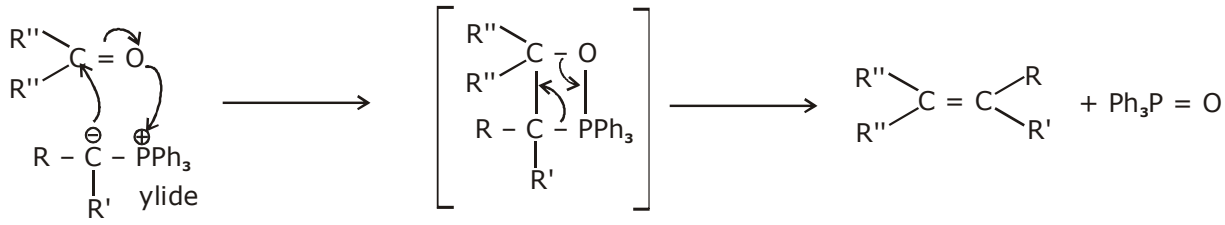




less crowded 'H'

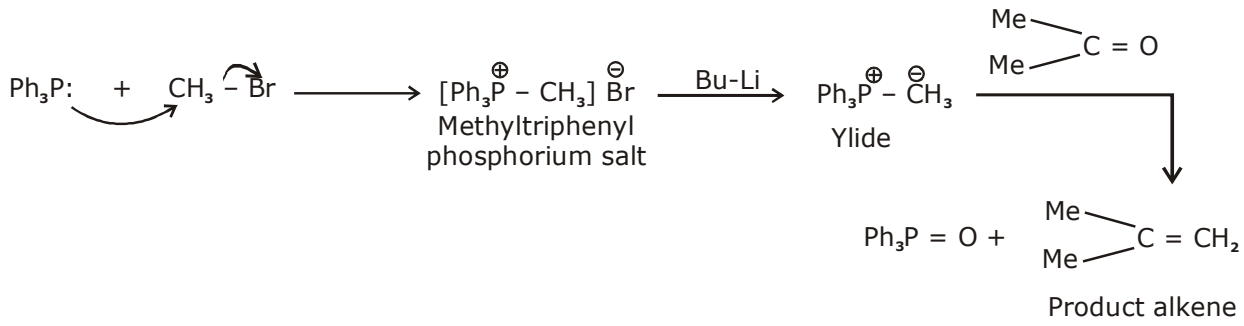
(VII) BY WITTIG REACTION

The aldehydes and ketones are converted into alkenes by using a special class of compounds called phosphorus ylides, also called Wittig reagents.
The Triphenyl group of phosphorane has a strong tendency to pull oxygen atom of the aldehyde or ketone via a cyclic transition state forming an alkene.

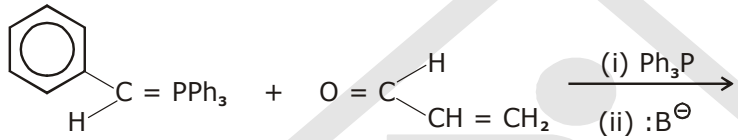


(R, R′, R″ and R‴ may be hydrogen or any alkyl group)

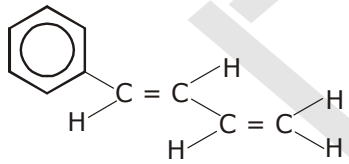
e.g.



Ex.7 Complete the following reaction :



Ans.



Ex.8 Identify the (X), (Y), and (Z) in the following reactions

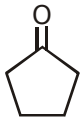
(i) $PhCH_2Br + CH_3 - \overset{O}{\overset{\|}{C}} - CH_3 \xrightarrow[(ii)\ :B^{\ominus}]{(i)\ Ph_3P} (X)$

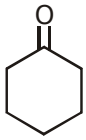
(ii) $CH_3I + PhCOCH_3 \xrightarrow[(ii)\ :B^{\ominus}]{(i)\ Ph_3P} (Y)$

(iii) $PhCH_2Br + PhCH = CHCHO \xrightarrow[(ii)\ :B^{\ominus}]{(i)\ Ph_3P} (Z)$

Ans. (X) = Ph – CH = $C(CH_3)_2$
(Y) = Ph – $C(CH_3)$ = CH_2
(Z) = Ph – CH = CH – CH = CH – Ph

Q.3 Complete the following reactions

(i) CH_3I +  $\xrightarrow[(ii)\ :B^{\ominus}]{(i)\ Ph_3P}$

(ii) C_2H_5Br +  $\xrightarrow[(ii)\ :B^{\ominus}]{(i)\ Ph_3P}$

6. Chemical reactions of alkenes

(I) CATALYTIC HYDROGENATION OF ALKENES : (HETEROGENEOUS HYDROGENATION)

Hydrogenation : The function of catalyst

Hydrogenation of a alkene is exothermic reaction (ΔH^o = – 120 kJ mol^{-1})

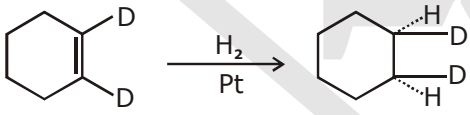
$$R - CH = CH - R + H_2 \xrightarrow{Ni} R - CH_2 - CH_2 - R + \text{heat}$$

As a consequence ,both hydrogen atoms usually add from the same side of the molecule. This mode of addition is called a **syn** addition.

Hydrogenation of an alkene is formally a reduction, with H_2 adding across the double bond to give an alkane.

The process usually requires a catalyst containing Pt, Pd or Ni.

e.g. $CH_3 - CH - = CH - CH_3 + H_2 \xrightarrow{Pt} CH_3 - CH_2 - CH_2 - CH_3$

e.g. 

Ex.9 Complete the following reactions :

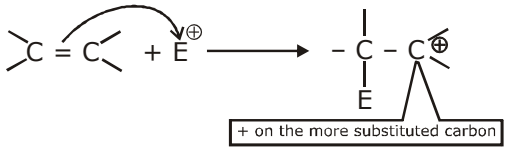
$$CH_3CH = CH_2 + H_2 \xrightarrow{Pd,Pt \text{ or } Ni} ?$$

Sol. $CH_3CH_2CH_3$

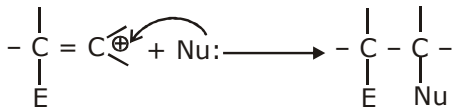
(II) ELECTROPHILIC ADDITION REACTIONS :

Mechanism

Step 1 : Attack of the electrophile on π bond forms a carbocation.



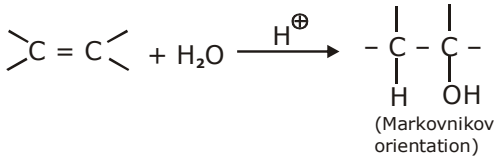
Step 2 : Attack by a nucleophile gives the product of addition



(i) Acid-Catalyzed Hydration of Alkenes

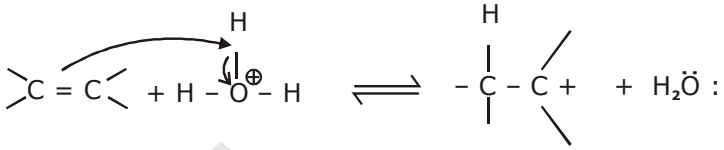
Alkenes add water in the presence of an acid catalyst to yield alcohols. The addition takes place with Markovnikov regioselectivity. The reaction is reversible, and the mechanism for the acid-catalyzed hydration of an alkene is simply the reverse of that for the dehydration of an alcohol. The carbocation intermediate may rearrange if a more stable carbocation is possible by hydride or alkanide migration. Thus, a mixture of isomeric alcohol products may result.

General Reaction

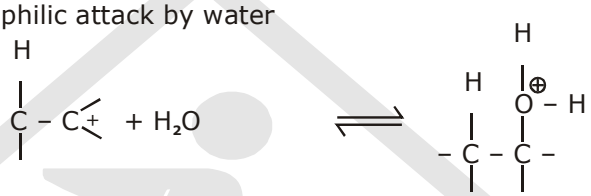


Mech.

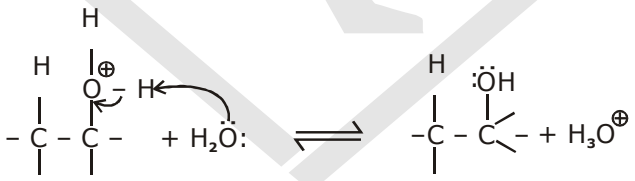
Step 1 : Protonation of the double bond forms a carbocation



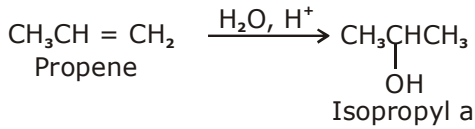
Step 2 : Nucleophilic attack by water



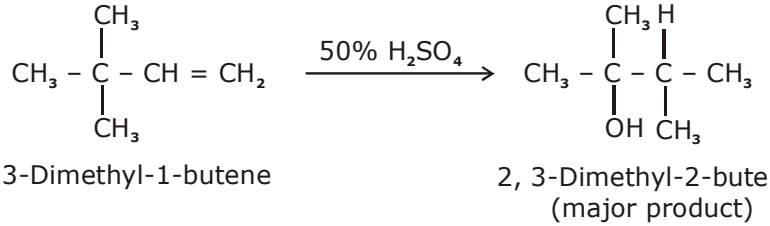
Step 3 : Deprotonation to the alcohol



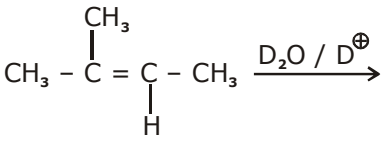
e.g.



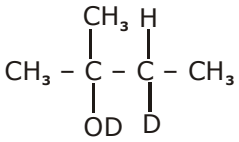
e.g.



Ex.10 Identify the product in following reaction



Ans.

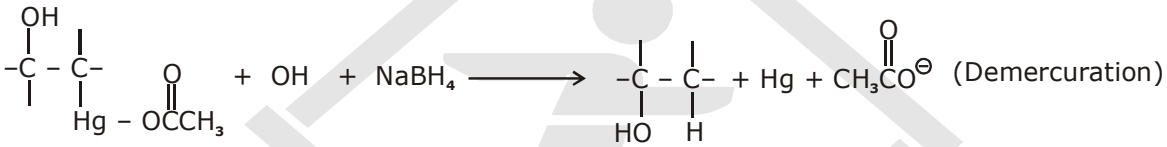


(ii) (a) Oxymercuration - Demercuration

Alkenes react with mercuric acetate in a mixture of water and tetrahydrofuran (THF) to produce (hydroxyalkyl) mercury compounds. These can be reduced to alcohols with sodium borohydride and water :

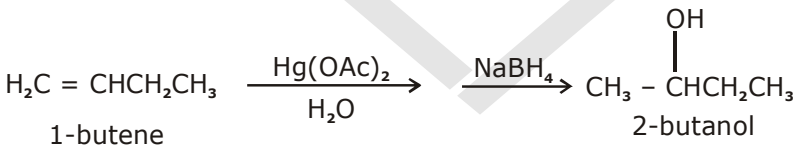
Oxymercuration

General Reaction



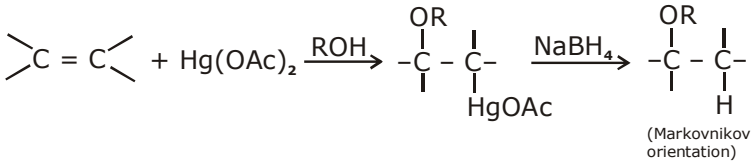
In the oxymercuration step, water and mercuric acetate add to the double bond; in the demercuration step, sodium borohydride reduces the acetoxymercury group and replaces in with hydrogen. Then net addition of H –and –OH takes place with Markovnikov regioselectivity and generally takes place without the complication of rearrangements.

e.g.

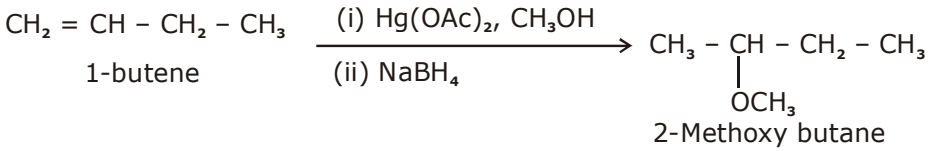


(b) Alkoxymercuration - demercuration

General reaction



e.g.

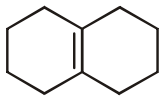


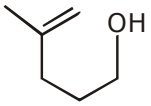
Ex.11 Supply the structures for (X) and (Y) in the following two – step reaction :

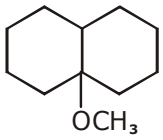
$$C_3H_7CH = CH_2 \xrightarrow[THF / H_2O]{Hg(OAC)_2} (X) \xrightarrow{NaBH_4 / NaOH} (Y)$$

Sol. (X) = $C_3H_7CH(OH)CH_2$–HgOAC (An organomercurial alcohol) (Y) = $C_3H_7CH(OH)CH_3$

Ex.12 Identify final product in the following :

(a)  $\xrightarrow[CH_3OH]{Hg(OAC)_2}$ $\xrightarrow{NaBH_4}$

(b)  $\xrightarrow{Hg(OAC)_2}$ $\xrightarrow[NaOH]{NaBH_4}$

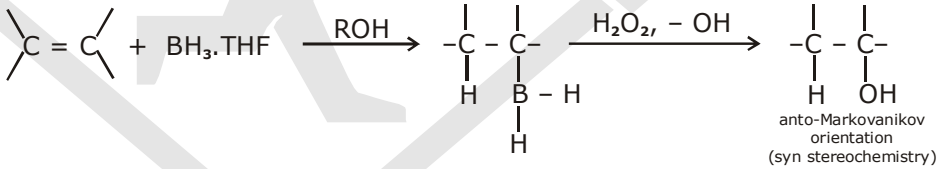
Ans. (a)  (b) 

Q.4 Identify the product in the following reaction

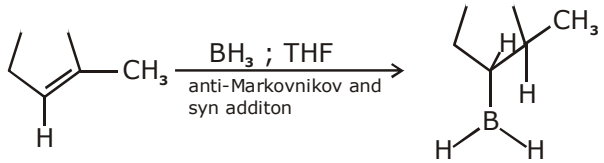
$$CH_3 - \underset{CH_3}{\overset{CH_3}{C}} - CH = CH_2 \xrightarrow{Hg(OAc)_2,\ H_2O} \xrightarrow{NaBH_4}$$

3, 3-Dimethyl - 1- butene

(iii) Hydroboration-oxidation (SYN ADDITION)

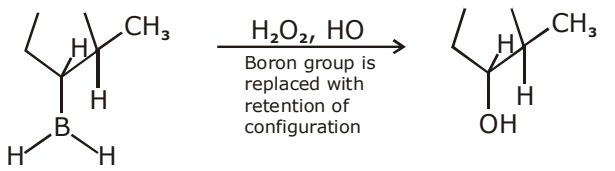
General Reaction 

An alkene reacts with BH_3 : THF of diborane to produce an alkylborane. Oxidation and hydrolysis of the alkylborane with hydrogen peroxide and base yields an alcohol.

e.g. 

+ enantiomer + dialkyl-and trialkylborane

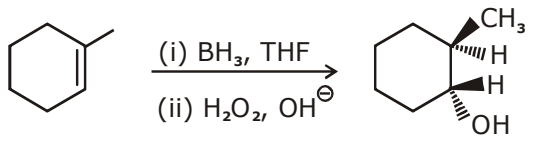
Oxidation



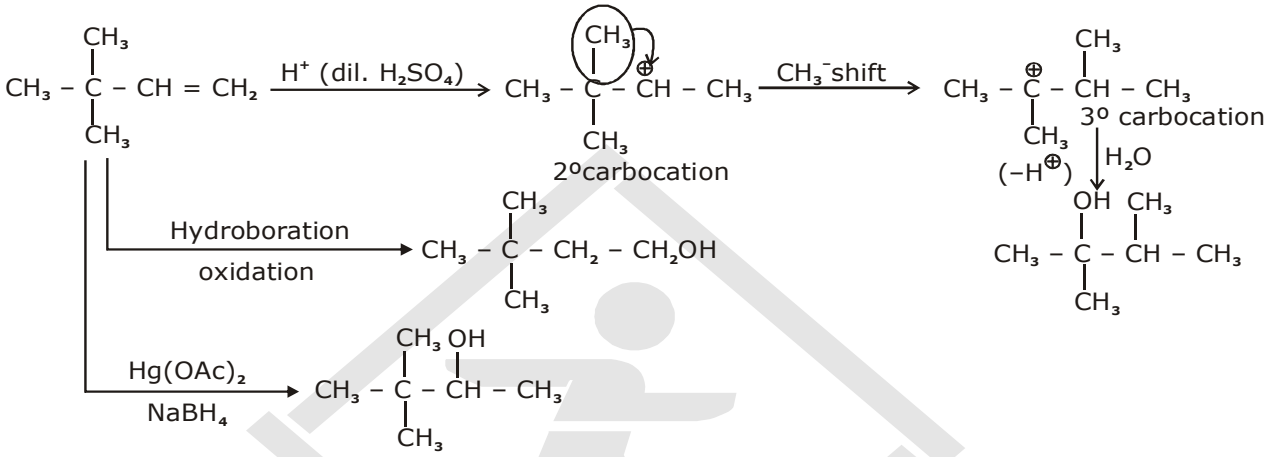
+ enantiomer

In the first step, boron and hydrogen undergo syn addition to the alkene in the second step, treatment with hydrogen peroxide and base replaces the boron with –OH with retention of configuration. The net addition of –H and –OH occurs with anti Markovnikov regioselectivity and syn stereoselectivity. Hydrogboration –oxidation therefore, serves as a useful regiochemical complement to oxymercuration demercuration.

e.g.

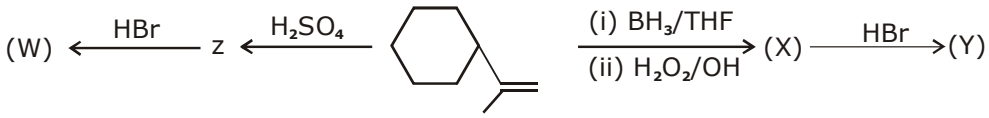


e.g.



(i) Hydration with dil. H_2SO_4 proceeds via carbocation rearrangement
(ii) Hydration with $Hg(OAc)_2$, H_2O, following by $NaBH_4$ proceeds via Markonikov's rule
(ii) Hydration with $(BH_3)_2$ followed by H_2O_2 / OH^- proceeds via Anti Markonikov's rule

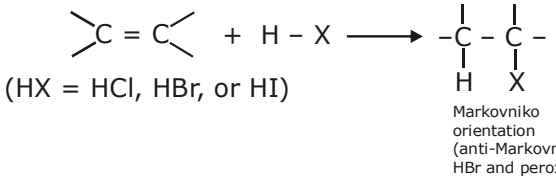
Q.5 Identify x, y, z and w in the following reaction :

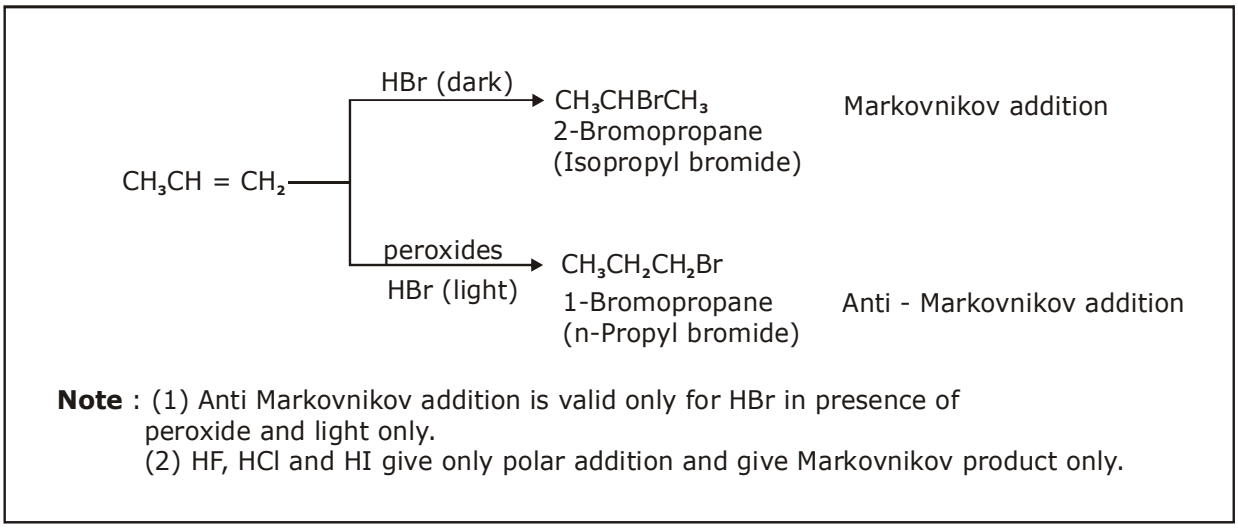


Also select pair of isomers if any

(iv) Addition of hydrogen halides

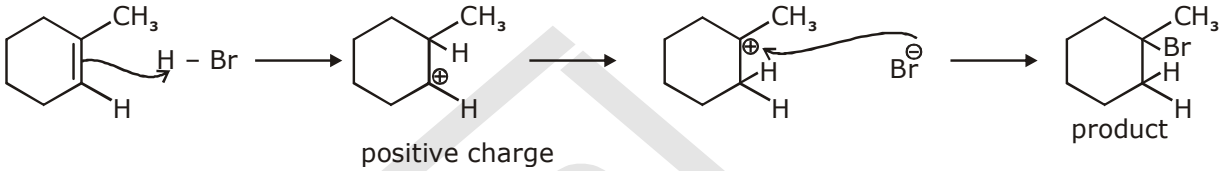
General Reaction





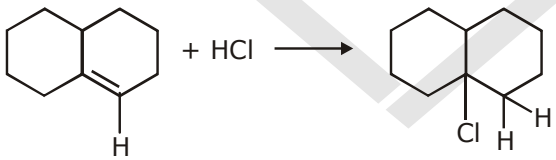
Note : (1) Anti Markovnikov addition is valid only for HBr in presence of peroxide and light only.
(2) HF, HCl and HI give only polar addition and give Markovnikov product only.

e.g. $CH_3CH = CH_2 \xrightarrow{HI} CH_3CHICH_3$
Propene — 2-Iodopropane (Isopropyl iodide)



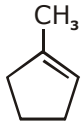
positive charge on less substituted carbon less stable ; not formed

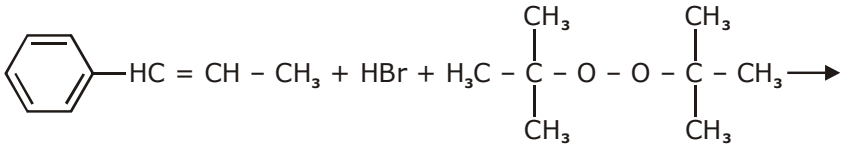
e.g.

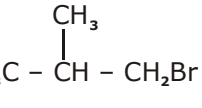
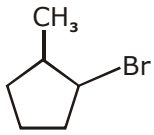
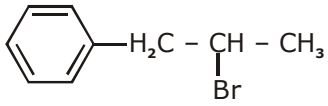


Ex.13 Predict the major products of the following reactions and propose mechanism to support your predictions.

(A) $H_3C - \underset{\displaystyle CH_3}{\overset{|}{C}} = CH_2 + HBr + CH_3 - \overset{\displaystyle O}{\overset{\|}{C}} - O - O - \overset{\displaystyle O}{\overset{\|}{C}} - CH_3 \longrightarrow$

(B)  $+ HBr + CH_3 - CH_2 - O - O - CH_2 - CH_3 \longrightarrow$

(C) 

Sol. (A)  (B)  (C) 

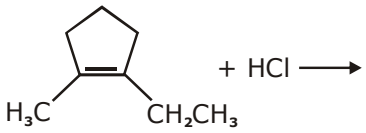
Ex.14 Identify the products in the following reactions :

(a) $F_3C - CH = CH_2 + HCl \longrightarrow$

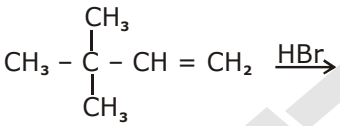
(b) $O_2N - CH = CH_2 + HCl \longrightarrow$

(c) $CH_3O - CH = CH_2 + HCl \longrightarrow$

(d) $PhCH = CHCH_3 + HCl \longrightarrow$

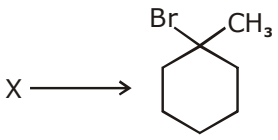
(e) 

Q.6 Give the products of the following reactions : –

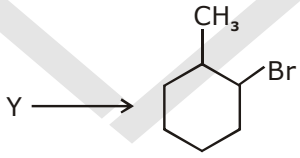


3, 3-dimethyl - 1 - butene

Q.7 Give the reactant (alkene) of the following products.



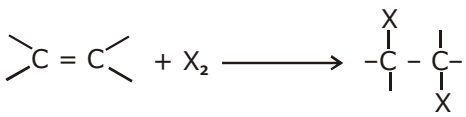
1-bromo-1-methyl cyclohexane



2-bromo-1-methyl cyclohexane

(v) Addition of halogen

Halogen add to alkenes to form vicinal dihalides.

General Reaction 

usually anti addition

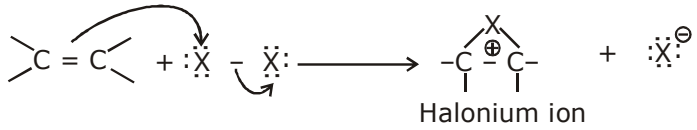
($X_2 = Cl_2, Br_2$)

The nucleophile attacks the electrophilic nucleus of one halogen atom, and the other halogen serves as the leaving group, departing as halide ion. Many reactions fit this general pattern.

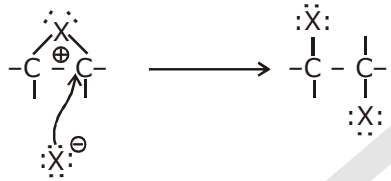
Note : (i) F_2 is not added because F^+ is never generated. Morever reaction is explosive giving CO_2 & H_2O
(ii) I_2 is not added because reaction is reversible with equilibrium in backward direction.
(iii) Reaction with bromine is basis for test of alkenes.
(iv) Halogen addition is stereospecific anti addition
(v) Halogens can also be added in presence of sun light and give free radical addition.
(Reactivity of halogen addition in sunlight is F_2 (explosive) > Cl_2 > Br_2 > I_2)

Mech.

Step-1 Formation of a halonium ion



Step-2 Opening of the halonium ion

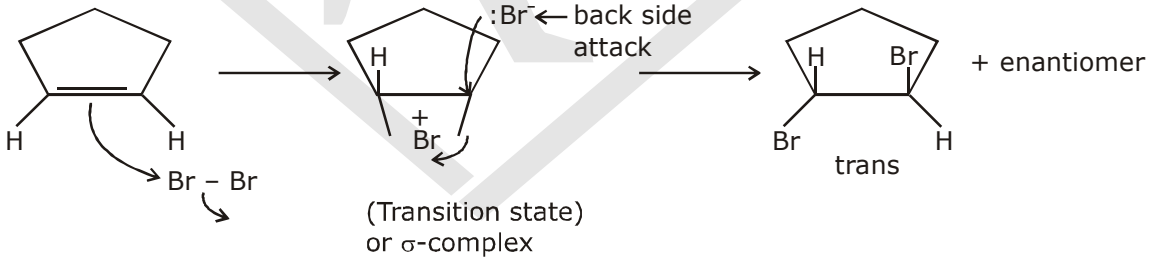


$X^{\ominus}$ attacks from the back side of halonium ion.

e.g. $CH_3CH = CH_2 \xrightarrow{Br_2 \text{ in } CCl_4} CH_3CHBrCH_2Br$

Propene (Propylene) — 1,2-Dibromopropane (Propylene bromide)

e.g.

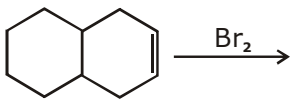


Ex.15 Give the product of the following reaction.

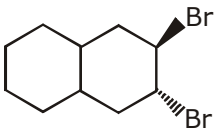
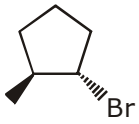
$Me_2C = CH_2 + ICl \rightarrow ?$

Sol. Cl is more electronegative than I making I the E^+ that, according to the Markovnikov rule, adds to the C with the greater number of H's. The product is 2-chloro-1-iodo-2-methylpropane, (Me_2CClCH_2I).

Ex.16 What are the products and (type of isomers) when Br_2 adds to : -

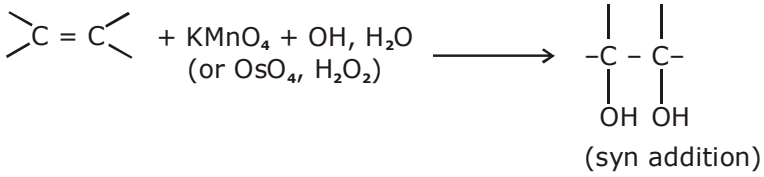
(a)  $\xrightarrow{Br_2}$

(b)  $\xrightarrow{Br_2}$

Ans. (a)  & enantiomer (b)  & enantiomer

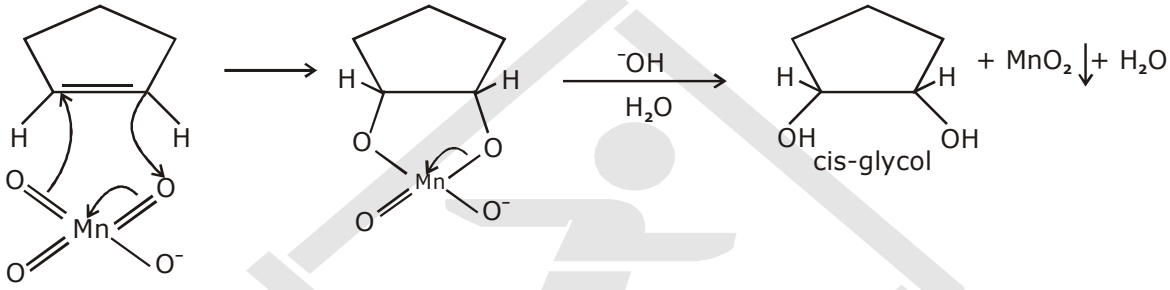
(vi) Hydroxylation of Alkenes

(a) Syn Hydroxylation : (Reaction with Bayer's reagent, (cold dilute alkaline $KMnO_4$ solution).
Both OH groups are added from same stereochemical side. This addition is example of syn addition

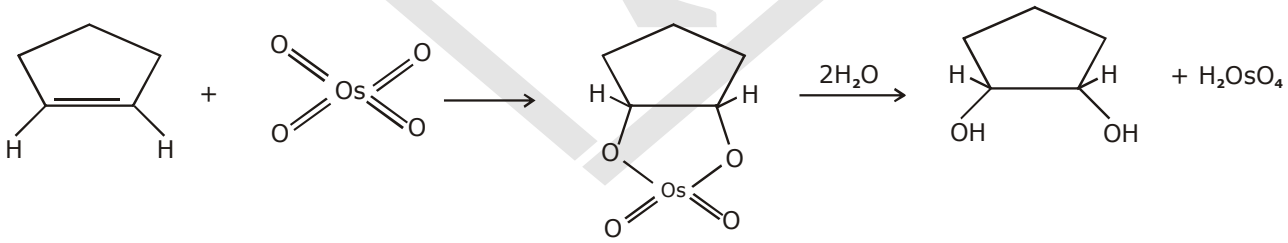
General Reaction 

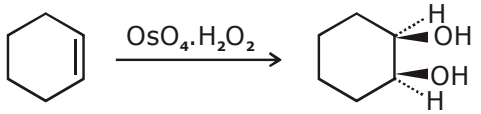
(syn addition)

e.g.



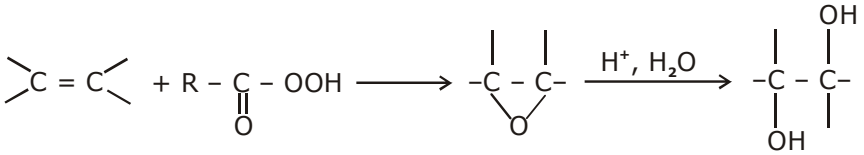
The same function of syn addition of 2 - OH groups is performed by OsO_4 / H_2O_2



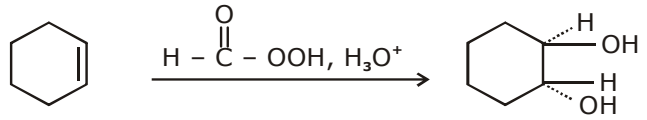
e.g. 

Cyclohexene Cis-Cyclohexane-1,2-diol

(b) Anti hydroxylation

General Reaction 

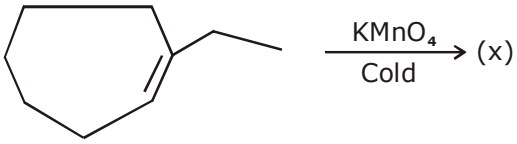
(anti addition)

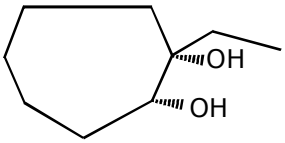
e.g. 

Cyclohexene

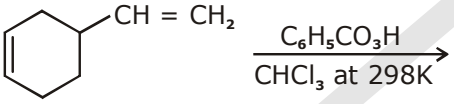
Trans-Cyclohexane-1,2-diol

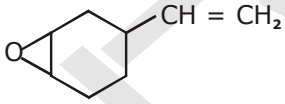
Ex.17 Identify the product in the following reaction :



Ans. 

Ex.18 Identify the product (X) in the following reaction :

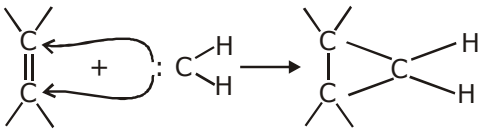


Ans. (x) : 

Since C = C bond in ring is more substituted than that in open chain.

(vii) Addition of carbenes to Alkenes :

Methylene is the simplest of the carbenes : uncharged, reactive intermediates that have a carbon atom with two bonds and two nonbonding electrons. Like borane (BH_2), methylene is a potent electrophile because it has an unfilled octet. It adds to the electrons rich pi-bond of an alkene to form a cyclopropane.

General Reactions 

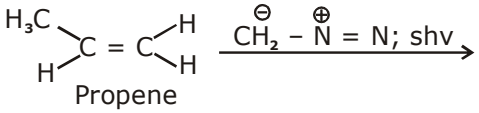
Heating or photolysis of diazomethane (CH_2N_2) gives nitrogen gas and methylene.

diazomethane

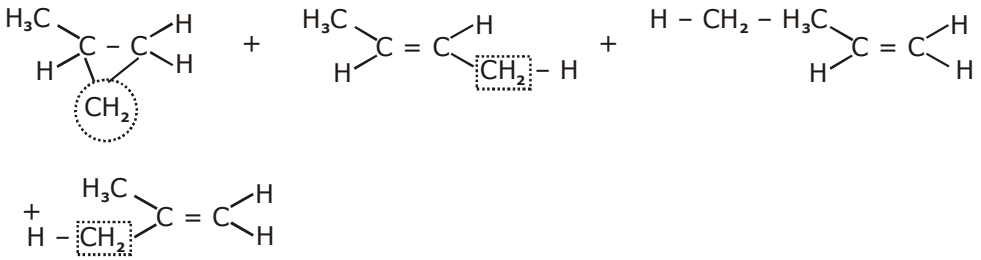
Methylene

There are two difficulties with using CH_2N_2 to cyclopropene double bonds. First, it is extremely toxic and explosive. A safer reagent would be more convenient for routine use. Second, methylene generated from CH_2N_2 is so reactive that it inserts into C – H bonds as well as C = C bonds.

e.g.



Propene

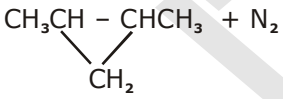


Ex.19 Identify the product in the following reactions

(a) $CH_3CH = CHCH_3$ + CH_2N_2 $\xrightarrow{light}$

2-Butene Diazomethane

(b)  + $CHBr_3$ $\xrightarrow{NaOH\ /H_2O}$

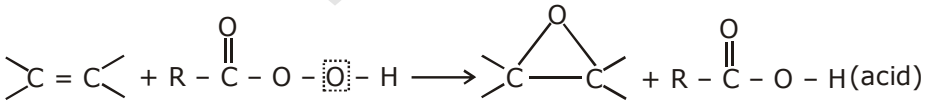
Ans. (a) 

1,2-Dimethylcyclopropene

(b) 

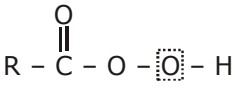
(III) EPOXIDATION OF ALKENES :

An alkene is converted to an epoxide by a peroxyacid, a carboxylic acid that has an extra oxygen atom in a –O – O – (peroxy) linkage.

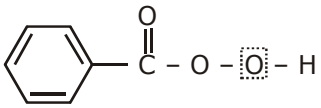
General Reaction 

Epoxide (Oxirane)

The epoxidation of an alkene is clearly an oxidation, since an oxidation, since an oxygen atom is added Peroxyacids are highly selective oxidizing agents. Some simple peroxyacids (sometimes called per acids) and their corresponding carboxylic acids are shown below :

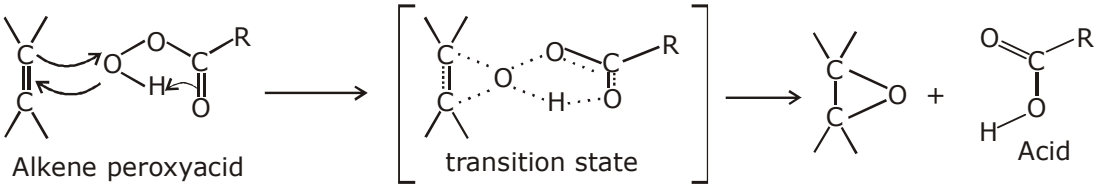


a peroxyacetic acid

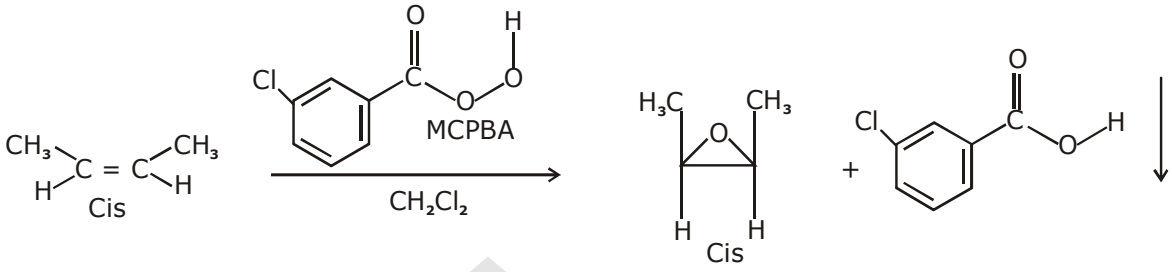


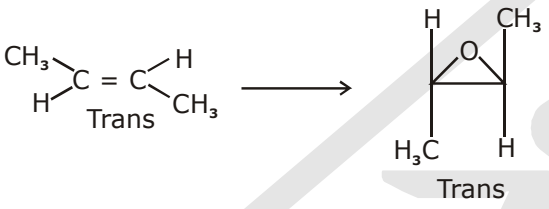
Peroxy benzoic acid

Mech.

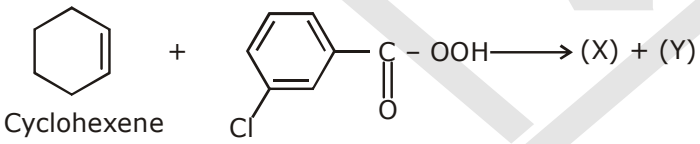


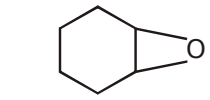
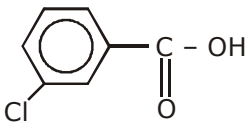
e.g.



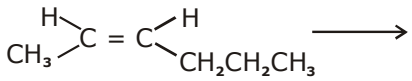


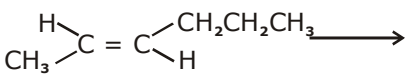
Ex.20 Complete the following reaction



Ans. (X)  Epoxycyclohexane (Y) 

Ex.21 Predict the product, including stereochemistry where appropriate, for the m-chloroperoxy-benzoic acid expoxidations of the following alkenes.

(a) 

(b) 

(c) Cis-cyclodecene ⟶

(D) Trans-cyclodecene ⟶

(IV) HALOHYDRIN FORMATION

General Reaction $-\overset{|}{C}=\overset{|}{C}- + X_2 + H_2O \longrightarrow -\underset{X}{\overset{|}{C}}=\underset{OH}{\overset{|}{C}}- + HX \quad (X_2 = Cl_2, Br_2)$

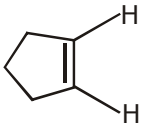
X' and H_2O are generated as attacking species from $X_2 + H_2O$

e.g. $CH_3CH = CH_2 \xrightarrow{Cl_2, H_2O} CH_3\underset{OH}{CH} - \underset{Cl}{CH_2}$

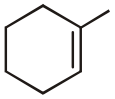
Propylene (Propene)

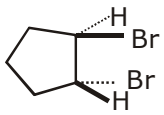
Propylene chlorohydrin (1-Chloro-2-propanol)

Ex.22 Predict the product in the following reactions

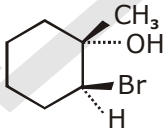
(a)  $\xrightarrow{Br_2}$ $\xrightarrow[\text{Anti addition}]{H_2O}$ (Markovnikov Orientation)

Cyclopentene

(b)  $+ Br_2 \xrightarrow[\text{Anti addition}]{H_2O}$ (Markovnikov Orientation)

Ans. (a) 

trans-1,2-dibromocyclo pentane (92%)

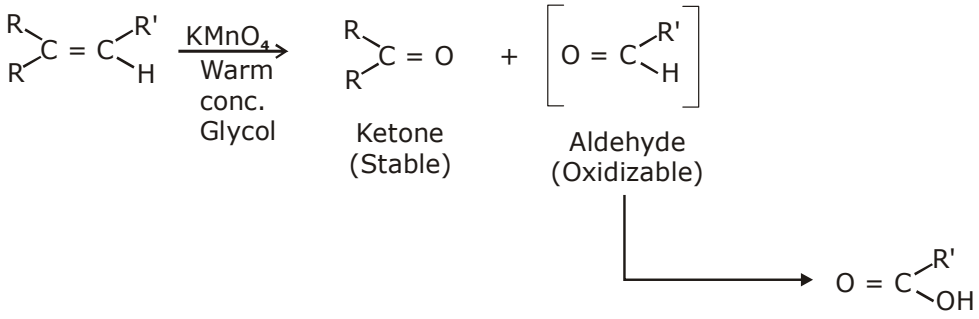
(b) 

(V) OXIDATIVE CLEAVAGE OF ALKENES

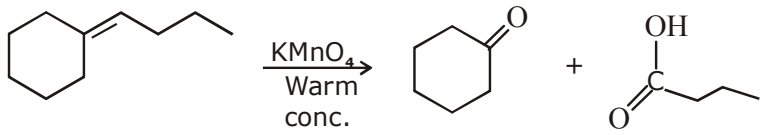
(i) Cleavage by permanganate

In a $KMnO_4$ hydroxylation, if the solution is warm or acidic or too concentrated, oxidative cleavage of the glycol may occur. Mixtures of Ketones and carboxylic acids are formed, depending on whether there are any oxidizable aldehydes in the initial fragments. A terminal = CH_2 group is oxidized to CO_2 and water.

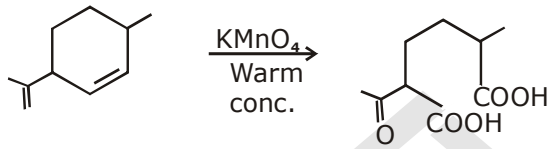
General Reaction



e.g.



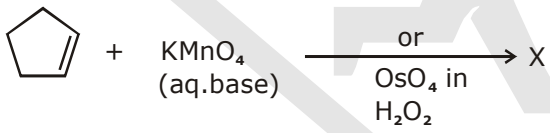
e.g.

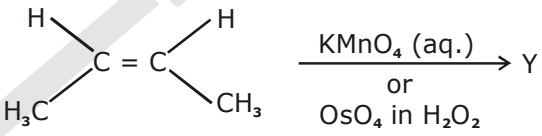


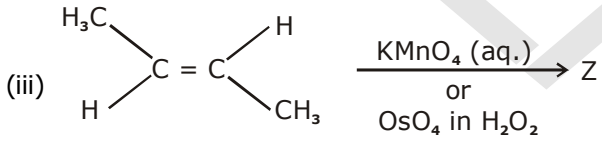
Ex.23 What is the main utility of this reaction and why is it superior to $KMnO_4$ cleavage for this purpose

Sol. It locates the position of C = C's in molecules. $KMnO_4$ cleavage is more vigorous and can oxidiz other groups, i.e., OH.

Ex.24 Give the products of the following reactions : -

(i) 

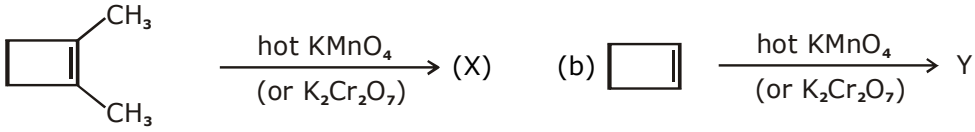
(ii) 

(iii) 

Sol. X = Cis-1, 2-Cyclopentanediol Y = meso - CH_3 – CHOH – CHOH – CH_3

Z = rac – $CH_3CHOHCHOHCH_3$

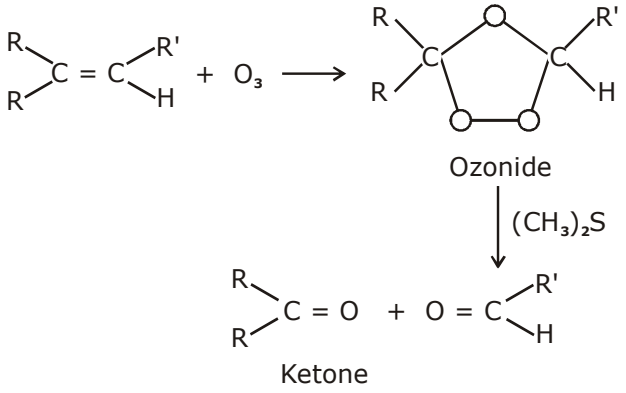
Q.8 Complete the following reactions

(a) 

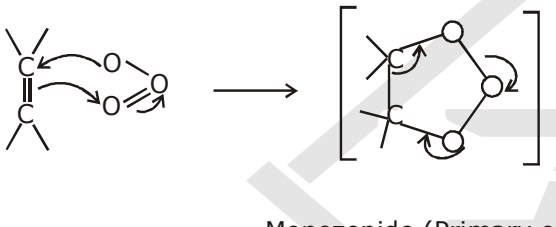
1,2-dimethylcyclobutene

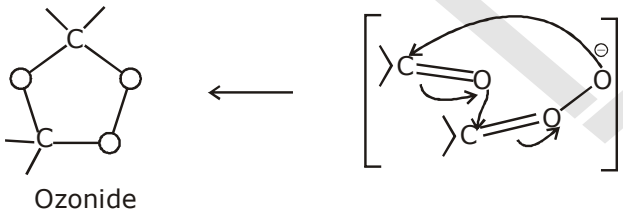
(ii) Ozonolysis : Like permanganate ozone cleaves double bonds to give ketones and aldehydes. However, ozonolysis is milder, and both ketones and aldehydes can be recovered without further oxidation.

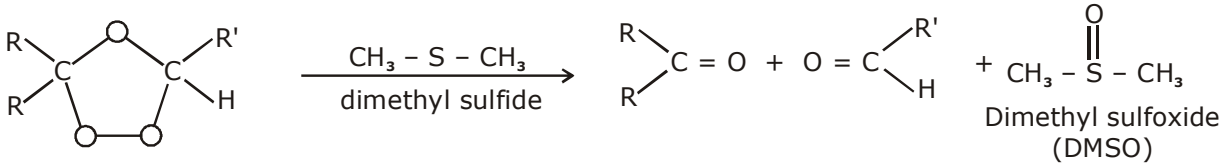
General Reaction



Mech.

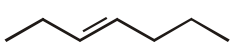






e.g. $CH_3CH_2CH = CH_2 \xrightarrow{O_3} \xrightarrow{H_2O,\ Zn} CH_3CH_2\underset{\displaystyle H}{\overset{\displaystyle |}{C}} = O + O = \underset{\displaystyle H}{\overset{\displaystyle |}{C}}H$

1-Butene

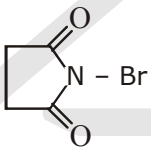
e.g.  3 - nonene $\xrightarrow[(ii)\ (CH_3)_2S]{(i)\ O_3}$ $CH_3CH_2CHO + CH_3(CH_2)_4CHO$ (65%)

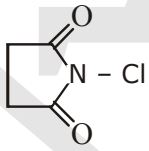
e.g. $CH_3-\underset{\displaystyle CH_3}{\overset{|}{C}}=CH_2 \xrightarrow{O_3} \xrightarrow{H_2O,\ Zn} CH_3\underset{\displaystyle CH_3}{\overset{|}{C}}=O + O=\underset{\displaystyle H}{\overset{|}{C}}H$

(VI) HALOGENATION, ALLYLIC SUBSTITUTION

General Reaction $H-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}=\overset{|}{\underset{|}{C}}-$ $\xrightarrow[(500\text{-}600^oC)]{X_2/\Delta}$ $X-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}=\overset{|}{\underset{|}{C}}-$; $\xrightarrow{NBS\ or\ NCS}$ $X-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}=\overset{|}{\underset{|}{C}}-$ $X_2 = Cl_2, Br_2$

(allyl halide)

NBS = N-Bromosuccinimide 

NCS = N-Chlorosuccinimide 

e.g. $CH_3CH=CH_2 \xrightarrow[600^oC]{Cl_2} Cl-CH_2CH=CH_2$

Propylene (Propene) — allyl chloride (3-Chloro-1-propene)

Ex.25 $CH_2=CHCH_2CH=CH_2 \xrightarrow{NBS}$ (X), (X) is

(A) $CH_2=CH-\underset{\displaystyle Br}{\overset{|}{C}}H-CH=CH_2$ (B) $CH_2=CHC=CHCH_2Br$

(C) $CH_2=CHCH_2CH=CHBr$ (D) $CH_2=CHCH_2\underset{\displaystyle Br}{\overset{|}{C}}=CH_2$

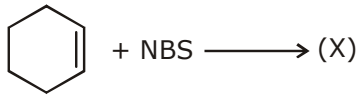
Ans. A

Ex.26 Assertion (A) : Propene ($CH_3CH = CH_2$) undergoes allylic substitution.

Reason (R) : $CH_2 = CHCH_2$ (allylic) free radical is stabilised by resonance.

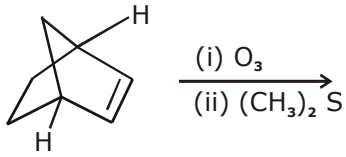
Ans. (A)

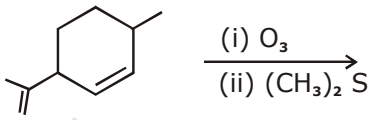
Q.9 Identify the product (X) in the following reaction

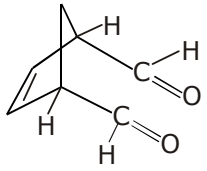


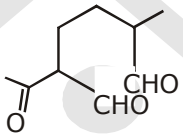
Cyclohexene

Ex.27 Identify the product in the following reactions

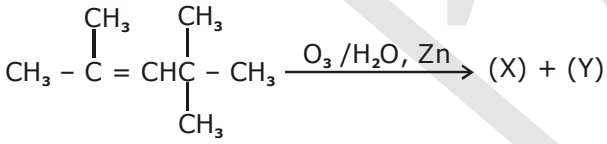
(a) 

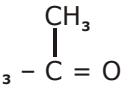
(b) 

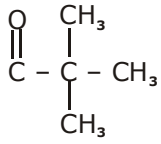
Ans. (a) 

(b) 

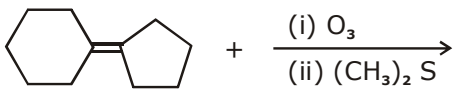
Ex.28 Identify the products (x, y) of following reaction : -



Ans. (X) : 

(Y) : 

Q.10 Predict the major product of the following reaction



(VII) ADDITION OF FREE RADICALS

General Reaction $-\overset{|}{C}=\overset{|}{C}- + Y-Z \xrightarrow[\text{or light}]{\text{peroxides}} -\overset{|}{\underset{Y}{C}}-\overset{|}{\underset{Z}{C}}-$

e.g. $n-C_6H_{13}CH=CH_2 \xrightarrow{BrCCl_3 \text{ peroxides}} n-C_6H_{13}\underset{Br}{CH}-CH_2-CCl_3$

1-Octene

3-Bromo-1,1,1-trichlorononane

$\xrightarrow{HBr/R_2O_2} n-C_6H_{13}CH-CH_2-Br$

Ex.29 Which of the following reactions are correct ?

(a) $C_6H_{13}CH=CH_2 + BrCCl_3 \xrightarrow{\text{peroxides}} C_6H_{13}\underset{Br}{CH}CH_2CCl_3$

(b) $RCH=CH_2 + BrCCl_3 \xrightarrow{\text{peroxides}} RCH\underset{Br}{CH_2}CCl_3$

(A) only (a) (B) only (b) (C) both are correct (D) None of these

Ans. (C)

Ex.30 Isobutylene $\xrightarrow[\text{peroxides}]{+HBr}$ product is :

(A) Tertiary butyl bromide (B) Isobutyl bromide

(C) Tertiary butyl alcohol (D) Isobutyl alcohol

Ans. (B)

ALKYNES

1. Introduction

A triple bond gives an alkyne four fewer hydrogen atoms than the corresponding alkane. There fore the triple bond contributes two degree of unsaturation (DU).

Alkynes are not as common in nature as alkenes, but some plants do use alkynes to protect themselves against disease or predators. Acetylene is by far the most important commercial alkyne. Acetylene is an important industrial feedstock but its largest use is as the fuel for the oxyacetylene welding torch.

2. Structure and Bonding in Alkynes

(1) Alkynes are hydrocarbons that contain carbon -carbon triple bond.

(2) Alkynes are also called acetylenes because they are derivatives of acetylene.

(3) The general formula is : C_nH_{2n-2}. (one triple bond)

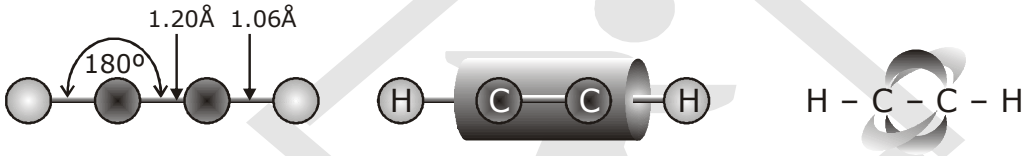
(4) In alkyne C ≡ C bond length is 1.20 Å.

(5) Its bond energy is 192 kcal. mol^{-1}

(6) The hybridization of carbon atoms having triple bond (C ≡ C) in alkynes is sp

(7) Overlapping of these sp hybrid orbitals with each other and with the hydrogen orbitals gives the sigma bond framework which is linear (180º) structure.

(8) Two π bonds result from overlap of the two remaining unhybridized p orbitals on each carbon atom. These orbitals overlap at **right angles** (90º) to each other, forming one π bond with electron density above and below the C – C sigma bond, and the other with electron density in front and in back of the sigma bond. This result in a cylindrical π electron cloud around σ bonded structure



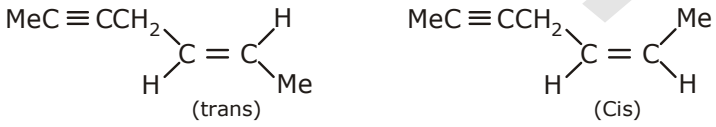
Note : Any type of stereoisomerism does not arise in acetylenic bond due to linearity of C ≡ C bond.

Ex.1 Cis-trans isomerism is not possible in alkynes because of :

Ans. 180º bond-angle at the carbon-carbon triple bond.

Ex.2 Draw the geometrical isomers of hept -2-en-5-yne?

Ans.



Q.1 C_6H_{10} (alkyne) is optically active. What is its structure?

Q.2 C_5H_8 (alkyne) has three-degree of unsaturation. What is the structure ? What is the isomerism show?

3. Physical Properties of Alkynes

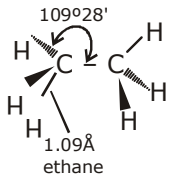
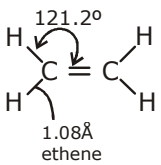
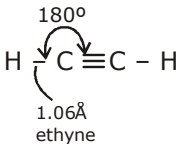
(1) Alkynes are relatively nonpolar (w.r.t. alkyl halides and alcohols) and are nearly insoluble in water (but they are more polar than alkenes and alkanes). They are quite soluble in most organic solvents, (acetone, ether, methylene chloride, chloroform and alcohols).

(2) Acetylene, propyne, and the butynes are gases at room temperature, just like the corresponding alkanes and alkenes. In fact, the boiling point of alkynes are nearly the same as those of alkanes and alkenes with same number of carbon atoms.

4. Table

Name	Formula	M.p.,°C	B.P., °C	Relative density (at 20°C)
Acetylene	$HC \equiv CH$	– 82	– 75	
Propyne	$HC \equiv CCH_3$	– 101.5	– 23	
1-Butyne	$HC \equiv CCH_2CH_3$	– 122	9	
1-Pentyne	$HC \equiv C(CH_2)_2CH_3$	– 98	40	0.695
2-Butyne	$CH_3C \equiv CCH_3$	– 24	27	0.694
2-Pentyne	$CH_3C \equiv CCH_2CH_3$	– 101	55	0.714
3-Methyl-1-butyne	$HC \equiv CCH(CH_3)_2$		29	665

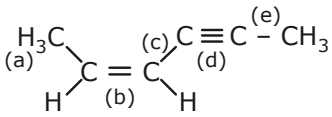
5. TABLE - COMPARATIVE STUDY OF ALKANES, ALKENES, ALKYNES

S.No.	Properties	Alkanes	Alkenes	Alkynes
1.	Bond length	1.54 (C – C)	1.32 (C = C)	1.20 (C ≡C)
2.	Bond energy ($KJmol^{-1}$)	415 (C – C)	615 (C = C)	835 (C ≡C)
3.	Hybridization	sp^3	sp^2	sp
4.	% s character	25%	33%	50%
5.	pKa	50	44	25
6.	Electronegativity of 'C'	→	Increases	→
7.	Polarity	→	Increases	→
8.	Rate of hydrogenation		less	more
9.	Rate of electrophilic addition reaction		more	less
10.	Heat of combustion	C_2H_6(-373)	C_2H_4(-337k cal)	C_2H_2(-317kcal)
11.	Density (g/cm^3)	C_3H_8(-373)	C_3H_6(0.52k cal)	C_3H_4(0.67)
12.	Structure			
13.	Shape	Tetrahedral	Planar	Linear

Ex.3 Which has a longer carbon-methyl bond, 1-butyne or 2-butyne. Explain?
Ans. The bond from the methyl group in 1-butyne is to an sp^3-hybridised carbon and so is longer than the bond from the methyl group in 2-butyne, which is to an sp-hybridised carbon.

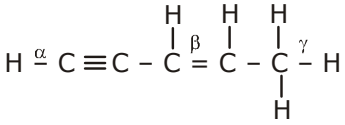
$CH_3-CH_2-C\equiv CH$ $CH_3-C\equiv C-CH_3$
sp^3 sp^3 sp^3 sp

Ex.4 Arrange the following bond-lengths in increasing order.



Ans. (d) < (b) < (c) < (e) < (a)

Q.3 Arrange C – H bond -lengths (α,β,γ) in increasing order as shown : –

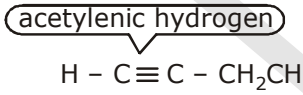


6. Laboratory test of Alkyne

Functional Group	Reagent	Observation	Reaction	Remarks
$-C\equiv C-$	(1) Bayer's Reagent alk.dil.cold $KMnO_4$	Pink Colour disappears	$HC\equiv CH + H_2O + O \xrightarrow{\text{alk. } KMnO_4} OHC-CHO$	Hydroxylation
	(2) Br_2/H_2O	Red Colour decolourises	$Br_2 + HC\equiv CH \rightarrow CHBr_2-CHBr_2$ (White ppt)	Bromination
	(3) O_3 (ozone)	Acid Formed	$R-C\equiv C-R' \xrightarrow{O_3} RCOOH + RCOOH$	Ozonolysis

7. Laboratory test of terminal alkynes

When triple bond comes at the end of a carbon chain. The alkyne is called a terminal alkyne.



1-Butyne, terminal alkyne

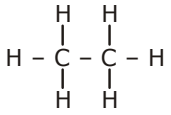
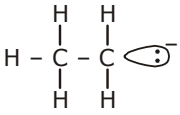
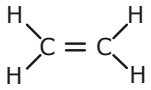
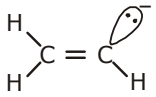
Functional Group	Reagent	Observation	Reaction
$R-C\equiv C-H$	(1) Cuprous chloride $+NH_4OH$	Red ppt.	$R-C\equiv CH + CuCl \xrightarrow{NH_4OH} R-C\equiv C\,Cu\downarrow$(red)
	(2) $AgNO_3 + NH_4OH$	White ppt	$R-C\equiv CH + Ag^+ \longrightarrow R-C\equiv C\,Ag\downarrow$(white)
	(3) Na in ether	Colourless gas	$HC\equiv CH + 2Na \longrightarrow Na-C\equiv C-Na + H_2\uparrow$

8. Acidity of Terminal Alkynes

Terminal alkynes are much acidic than other hydrocarbons due to more electronegative sp hybridised carbon. The polarity (acidity) of a C – H bond varies with its hydridization, increasing with the increase in precentage's character of the orbitals.

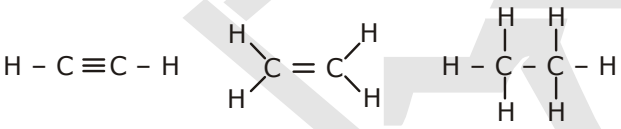
$sp^3 < sp^2 < sp$

Weakest acid

S.No.	Compound	Conjugate Base	Hybridization of C⁻	%Character	pK_a
1.			sp^3	25%	50
2.			sp^2	33%	44
3.	$:NH_3$	$:\ddot{N}H_2^-$			
4.	H – C≡C – H	H – C≡C:⊖	sp	50%	25
5.	R – OH	R – $\ddot{O}^-$			16-18

Stronger acid

The hydrogen bonded to the carbon of a terminal alkyne is considerably more acidic than those bonded to carbons of an alkene and alkane (see section). The pK_a values for ethyne, ethene & ethane illustrate this point



$pK_a = 25$ $pK_a = 44$ $pK_a = 50$

The order of basicity of their anions is opposite to that of their relative acidity:

Relative Basicity

$CH_3\overset{\ominus}{C}H_2 > H_2C = CH:^- > HC \equiv C:^-$

Relative acidity

$H - \ddot{O}H > H - \ddot{O}R > H - C \equiv CR > H - \ddot{N}H_2 > H - CH{=}CH_2 > H - CH_2CH_3$

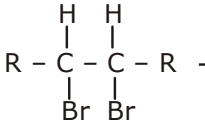
pK_a 15.7 16-17 25 38 44 50

Relative Basicity

$\overset{\ominus}{:}\ddot{O}H < \overset{\ominus}{:}\ddot{O}R < \overset{\ominus}{:}C \quad CR < \overset{\ominus}{:}\ddot{N}H_2 < \overset{\ominus}{:}CH = CH_2 < \overset{\ominus}{:}CH_2CH_3$

9. General methods of preparation :

(I) By dehydro halogenation of gem and vic dihalide:

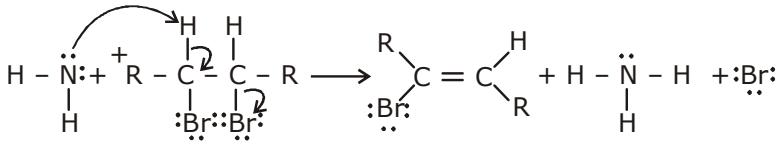
General Reaction: $RCH = CHR + Br_2 \rightarrow$  $\xrightarrow{2NaNH_2}$ $R - C \equiv C - R + 2NaBr$

A vic - dibromide

The dehydrohalogenations occur in two steps, the first yielding a bromoalkene and the second alkyne.

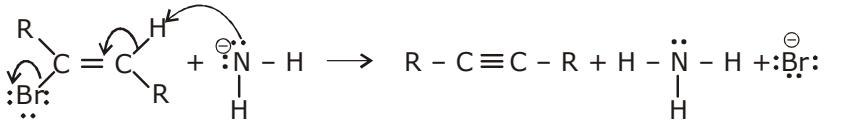
Mechanism :

Step 1



Amide ion (The strongly basic amide ion brings about an E2 reaction.) | Vic-Dibromide | Bromoalkene | Ammonia | Bromide ion

Step 2



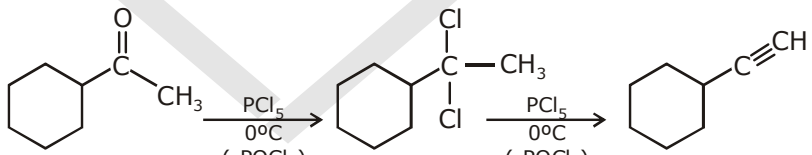
Bromoalkene (A second E2 reation produces the alkyne) | Amide ion | Alkyne | Ammonia | Bromide ion

e.g. $CH_3CH_2CH = CH_2 \xrightarrow[CCl_4]{Br_2} CH_3CH_2CHCH_2Br \xrightarrow[\text{mineral oil, } 110\text{-}160^oC]{NaNH_2} CH_3CH_2C \equiv CH$

e.g. $\left[\begin{matrix} CH_3CH_2CH=CHBr \\ + \\ CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}} = CH_2 \end{matrix}\right] \xrightarrow[\text{mineral oil, } 110\text{-}160^oC]{NaNH_2} [CH_3CH_2C \equiv CH] \xrightarrow{NaNH_2} CH_3CH_2C \equiv C^{\ominus}Na^{\oplus}$

$CH_3CH_2C \equiv C{:}^{-}Na^{+} \xrightarrow{NaNH_2} CH_3CH_2C \equiv CH + NH_3 + NaCl$

General Reaction

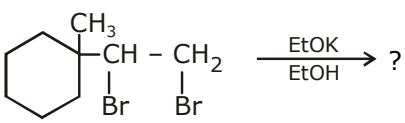


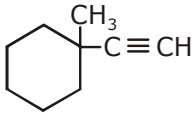
Cyclohexyl methyl Ketone | A gem-dichloride (70-80%) | Cyclohexylacetylene (46%)

Ex.5 Give the structure of three isomeric dibromides that could be used as starting materials for the preparation of 3,3-dimethyl-1-butyne.

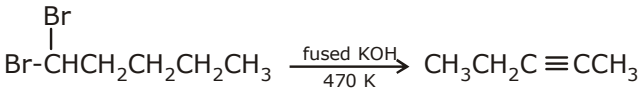
Sol. (I) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_2-CHBr_2$ (II) $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{C}}} - \underset{\displaystyle Br}{\overset{|}{CH}} - \underset{\displaystyle Br}{\overset{|}{CH_2}}$ (III) $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3\ Br}{\overset{|}{C}}} - \underset{\displaystyle Br}{\overset{|}{C}} - CH_3$

Ex.6 Show the product in the following reaction



Sol. 

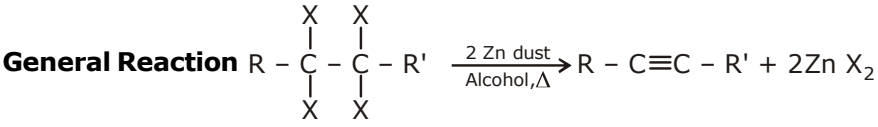
Q.4 1,1-dibromopentane on reaction with fused KOH at 470 K gives 2-pentyne



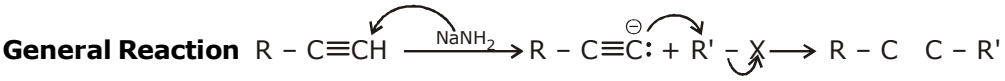
1,1-dibromo pentane 2-pentyne

Give the mechanism of this rearrangement.

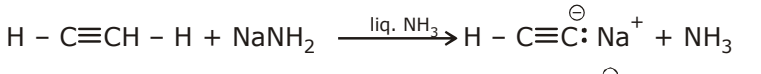
(II) By Dehalogenation of Tetrahaloalkane:

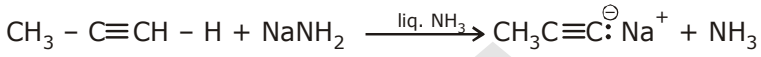
General Reaction 

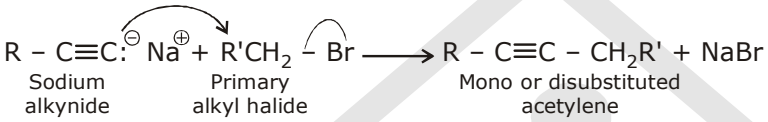
(III) Replacement of The Acetylenic Hydrogen atom of terminal Alkynes.

General Reaction 

Sodium ethynide and other sodium alkynides can be prepared by treating terminal alkynes with sodium amide in liquid ammonia.

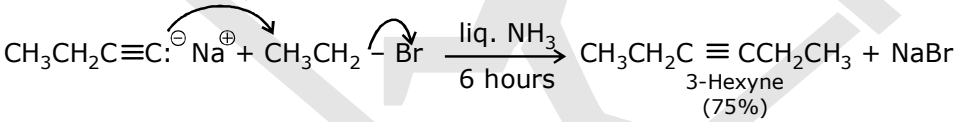


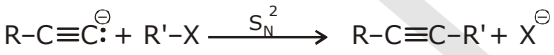




(R or R' or both may be hydrogen)

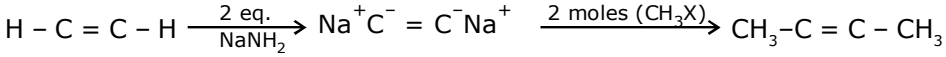
The following example illustrates this synthesis of higher alkyne homologues.

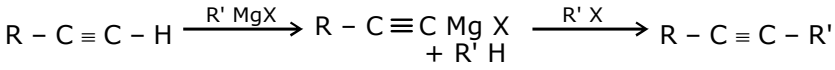


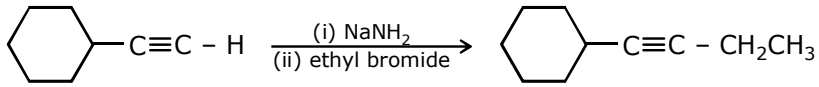


(R'–X must be an unhindered primary halide or tosylate)

The unshared electron pair of the alkynide ion attacks the back side of the carbon atom that bears the halogen atom and forms a bond to it. The halogen atom departs as a halide ion.

e.g. 

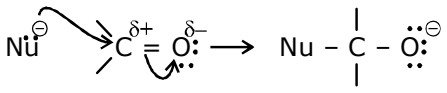
e.g. 

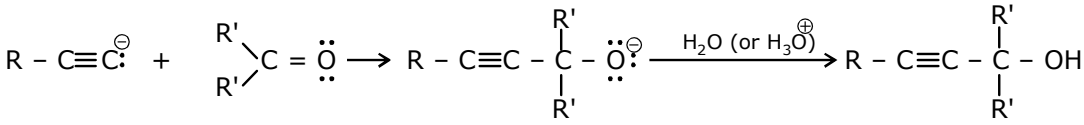
e.g. 

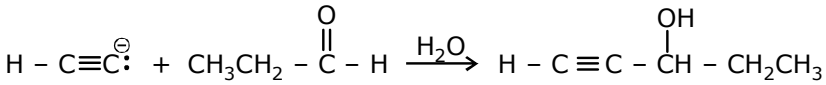
Ethynylcyclohexane

1-Cyclohexyl-1-butyne
(ethylcyclohexyl acetylene)

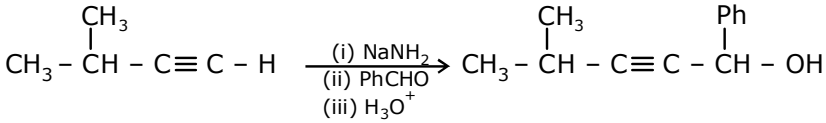
Addition of acetylide ions to carbonyl groups



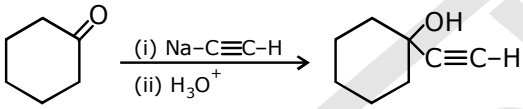


e.g. 

Sodium acetylide Propanal 1-Pentyn-3-ol

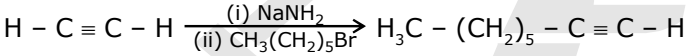
e.g. 

3-Methyl-1-butyne 4-Methyl-1-Phenyl pent-2-yne-1-ol

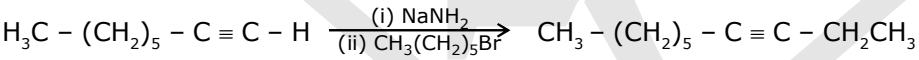
e.g. 

Cyclohexanone 1-Ethynylcyclohexanol(3º)

Ex.7 Show how to synthesize 3-decyne from acetylene along with necessary alkyl halides.

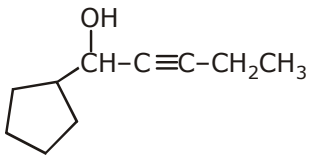
Sol. 

1-Octyne

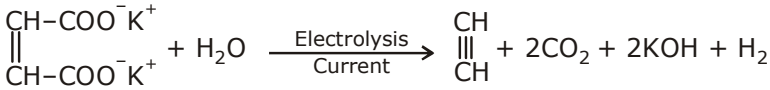


1–Octyne 3–Decyne

Q.5 Show how you would synthesize the following compound, beginning with acetylene and any necessary additional reagents.



(IV) By Kolble's Electrolytic synthesis.



(V) By Hydrolysis of carbides

$CaC_2 + 2HOH \rightarrow C_2H_2 + Ca(OH)_2$

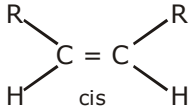
$MgC_2 + 2HOH \rightarrow C_2H_2 + Mg(OH)_2$

$Mg_2C_3 + 4HOH \rightarrow CH_3 - C \equiv CH + 2Mg(OH)_2$

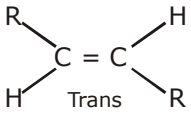
10. Chemical reactions of Alkyne

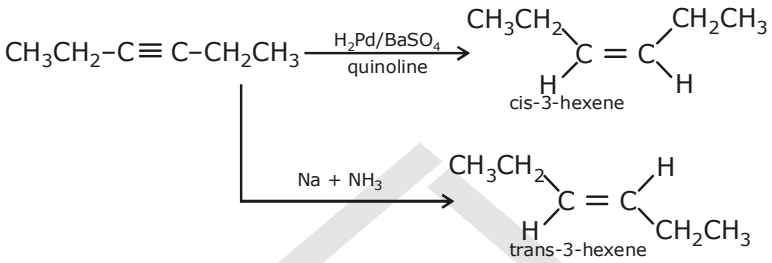
(I) Reduction to alkenes

(a) By Lindlar's reagent

General Reaction $R-C\equiv R' + H_2 \xrightarrow{Pd/BaSO_4,\ quinoline}$  (syn addition)

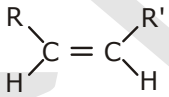
(b) By Brich reduction

General Reaction $R-C\equiv C-R' \xrightarrow{Na + NH_3}$  (anti addition)

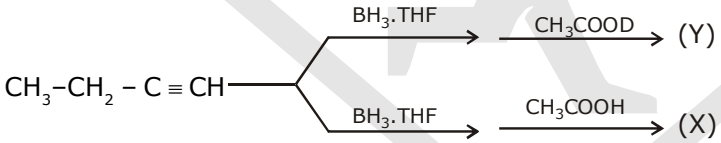


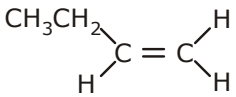
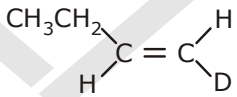
e.g.

(c) By hydroboration reduction

General Reaction $R-C\equiv C-R' \xrightarrow[(ii)\ CH_3COOH]{(i)\ BH_3-THF}$ 

Ex.8 Identify (X) and (Y) in the following reaction



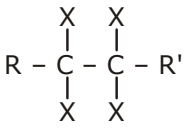
Ans. (X) :  (Y) : 

Q.6 Use two methods to convert 2-butyne to (z) – 2,3-dideutero-2-butene

Q.7 From 1–butyne, synthesize
(a) (E) –1-deutero-1-butene and
(b) 2-deutero -1-butene

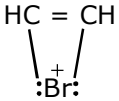
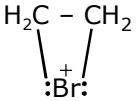
Q.8 Write the equation for the reduction of 2-butyne with Na with EtOH.

(II) Addition of Halogen (X_2=Cl_2, Br_2)

General Reaction $R-C\equiv C-R' \xrightarrow{X_2} R-CX=CX-R' \xrightarrow{X_2}$  (Anti-addition)

Ex.9 Explain why alkynes are less reactive than alkenes toward addition of Br_2.

Sol. The three memebered ring bromonium ion fromed from the alkyne (A) has a full double bond causing it to be more strained and less stable than the one from the alkene (B).

(A)  (B) 

(A) less stable than (B)

Also, the C's of A that are part of the bormonium ion have more s-character than those of B, further making A less stable than B.

(III) Addition of Hydrogen halides (Were HX = HCl, HBr, HI)

General Reaction $R-C\equiv C-R' \xrightarrow{H-X} \underset{\text{(Markovnikov addition)}}{R-CH=CX-R'} \xrightarrow{H-X} R-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{X}{C}}-R'$

e.g. $\underset{\text{1-Butyne}}{CH_3CH_2-C\equiv C-H} \xrightarrow{HCl} \underset{\text{2-Chloro-1-butene}}{CH_3CH_2-\underset{Cl}{\overset{}{C}}=\underset{H}{\overset{Cl}{C}}-H} \xrightarrow{HCl} \underset{\text{2,2-dichlorobutane}}{CH_3CH_2-\underset{Cl}{\overset{Cl}{C}}-CH_3}$

e.g. $CH_3-C\equiv C-CH_2CH_3 + HBr \rightarrow CH_3-\underset{}{\overset{Br}{C}}=\underset{H}{\overset{}{C}}-CH_2CH_3 + CH_3-\underset{}{\overset{H}{C}}=\underset{Br}{\overset{}{C}}-CH_2CH_3$

e.g. $H-C\equiv C-CH_2CH_2CH_3 \xrightarrow{HBr} \underset{H}{\overset{H}{C}}=\underset{Br}{\overset{CH_2CH_2CH_3}{C}} \xrightarrow{HBr} H-\underset{H}{\overset{H}{C}}-\underset{Br}{\overset{Br}{C}}-CH_2CH_2CH_3$

Ex.10 Identify the product when one equivalent of HBr reacts with 1-pentene-4-yne

Ans. $CH_2=CHCH_2C\equiv CH \xrightarrow{H^{\oplus}} \underset{\text{stable 2° alkyl carbocation}}{CH_3\overset{\oplus}{C}HCH_2C\equiv CH} \xrightarrow{Br} CH_3\underset{Br}{CH}CH_2C\equiv CH$

$CH_2=CHCH_2C\equiv CH \xrightarrow{H^{\oplus}} \underset{\text{less stable vinyl carbocation (It is not formed)}}{CH_2=CHCH_2\overset{\oplus}{C}=CH_2}$

Ex.11 $CH_3C\equiv CH \xrightarrow{2HBr} (X) + (Y)$

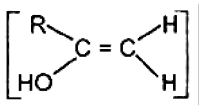
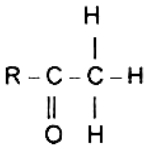
Idntify (X) and (Y) in the above reaction.

Ans. After first HBr molecule is added, product is $CH_3\underset{Br}{C}=CH_2$: Second addition $\underset{(2^o)}{CH_3-\underset{Br}{\overset{\oplus}{C}}-CH_3}$ and $\underset{(1^o)}{CH_3-\underset{Br}{C}-\overset{\oplus}{C}H_2}$.

Since 2º carbocation ion is more stable than 1º, hence final product is $\underset{(X)}{CH_3-\underset{Br}{\overset{Br}{C}}-CH_3}$ Y is $CH_3CH_2CHBr_2$

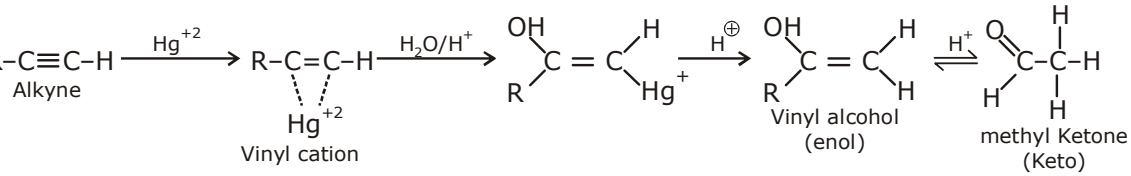
(IV) Addition of water

(a) Mercuric ion catalyzed hydration:

General Reaction $R - C \equiv C - H + H_2O \xrightarrow[\text{Dil. } H_2SO_4]{\text{Dil. } HgSO_4}$  $\underset{}{\overset{\text{Tauto.}}{\rightleftharpoons}}$ 

(Martkovnikov rule) Vinyl alcohol (unstable) Ketone (stable)

Electrophilic addition of mercuric ion gives a vinyl cation, which reacts with water and loses a proton to give an organomercurical alcohol. Under the acidic reaction condition, Hg is replaced by hydrogen to give a vinyl alcohol, callled an enol.

Mech. 

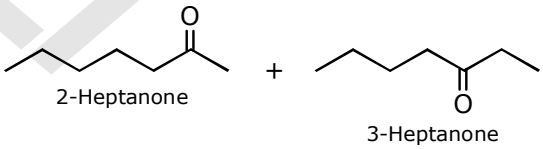
e.g. $CH_3 - C \equiv C - H + H_2O \xrightarrow[\text{Dil. } H_2SO_4]{\text{Dil. } HgSO_4} CH_3 - \overset{O}{\overset{\|}{C}} - CH_3$ Propanone (acetone)

Ex.12 $CH_3 - C \equiv CH + H_2O \xrightarrow[\text{Dil. } H_2SO_4]{\text{Dil. } HgSO_4} X$

Identify the (X) in the above reaction

Sol. (X) = $CH_3\overset{O}{\overset{\|}{C}}CH_3$ Acetone (a ketone) stable

Ex.13 When 2-heptyne was treated with aq. H_2SO_4containing some $HgSO_4$, two products, each having the moleuclar formual $C_7H_{14}O$, were obtained approximately in equal amounts. What are these two compounds?

Ans. $CH_3CH_2CH_2CH_2C \equiv CCH_3 \xrightarrow[\text{Dil. } H_2SO_4]{\text{Dil. } HgSO_4}$  +

2-Heptanone 3-Heptanone

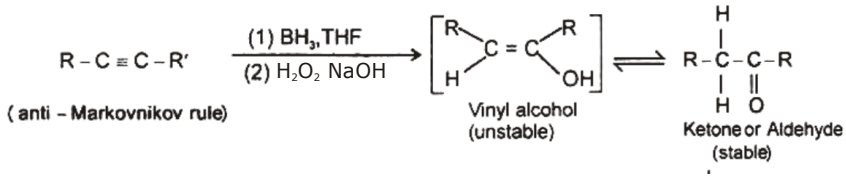
Q.9 From which alkyne could each of the following compound be prepared by acid-catalysed hydration?

(a) $CH_3\overset{O}{\overset{\|}{C}}CH_2CH_2CH_3$ (b) $(CH_3)_3\overset{O}{\overset{\|}{C}}CCH_3$ (c) $CH_3(CH_2)_3\overset{O}{\overset{\|}{C}}(CH_2)_4CH_3$

(b) Hydroboration-oxidation

In alkyne, except that a hindered dialkylborane must be used to prevent addition of two molecules of borane across the triple bond.

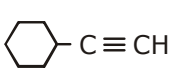
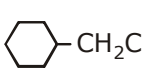
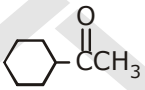
General Reaction



e.g. $CH_3-C\equiv C-H \xrightarrow[(2)\ H_2O_2,\ NaOH]{(1)\ BH_3,\ THF} CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H$
Propanal

Ex.14 Compare the results of hydroboration oxidation and mercuric ion-catalysed hydration for
(a) 2-butyne (b) Cyclohexyl-actylene

Ans.

Reactant	Product by	
	Hydroboration oxidation	Hg^{2+} ion-catalysed hydration
(a) $CH_3C\equiv CCH_3$	$CH_3\overset{O}{\overset{\|}{C}}CH_2CH_3$	$CH_3\overset{O}{\overset{\|}{C}}CH_2CH_3$
(b) 		

(V) Formation of Alkylide anions (Alkynides)
Sodium, lithium and magnesium alkynide

General Reaction $R-C\equiv C-H + NaNH_2 \rightarrow R-C\equiv C:^{-}\ {}^{+}Na + NH_3$

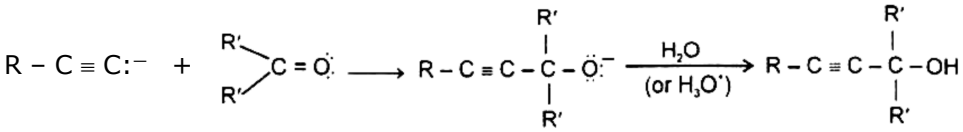
$R-C\equiv C-H + R'-Li \rightarrow R-C\equiv CLi + R'H$

$R-C\equiv C-H + R'MgX \rightarrow R-C\equiv CMgX + R'H$

(VI) Alkylation of alkylide ions
General Reaction $R-C\equiv C:^{-} + R'-X \rightarrow R-C\equiv C-R'$
(R' – X must be an unhindered primary halide or tosylate)

e.g. $CH_3CH_2\,C\equiv C^{-}\ {}^{+}Na + CH_3CH_2CH_2-Br \rightarrow CH_3CH_2-C\equiv C-CH_2CH_2CH_3$
sodium butynide 1-bromopropane Hept-3-yne

(VII) Reactions with Carbonyl Groups
General Reaction

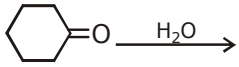


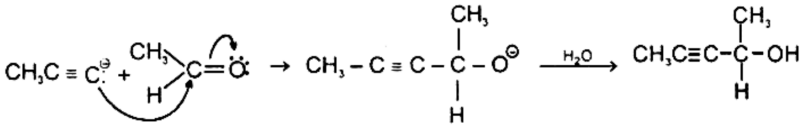
e.g. $CH_3-C\equiv C:^{-}Na^{+} \xrightarrow[(2)\ H_2O]{(1)\ CH_3CH_2-\overset{O}{\overset{\|}{C}}-CH_3} CH_3-C\equiv C-\underset{CH_3}{\overset{OH}{\overset{|}{\underset{|}{C}}}}-CH_2CH_3$
sodium propynide
3-methyl hex-4-yn-3-ol

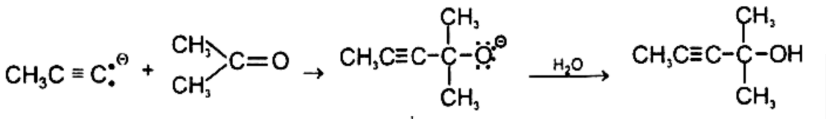
Ex.15 Give the products of the following reactions.

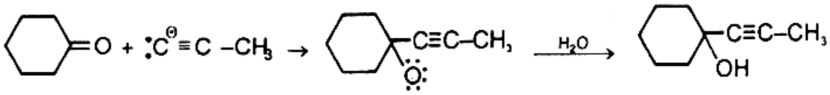
(a) $CH_3C \equiv C^{\ominus}: + CH_3CH = O \xrightarrow{H_2O} X$

(b) $CH_3C \equiv C^{\ominus}: + (CH_3)_2C = O \xrightarrow{H_2O} Y$

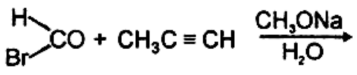
(c) $CH_3C \equiv C^{\ominus}: +$  $\xrightarrow{H_2O} Z$

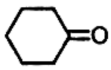
Sol. (a) 

(b) 

(c) 

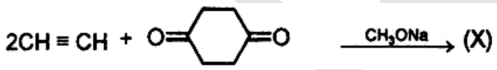
Q.10 What are the products of the following reactions:

(a) 

(b) $CH_3C \equiv CH +$  $\xrightarrow[H_2O]{CH_3ONa}$

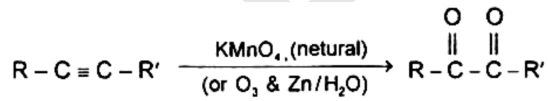
(c) $HC \equiv CD + CH_3CHO \xrightarrow[H_2O]{CH_3ONa}$

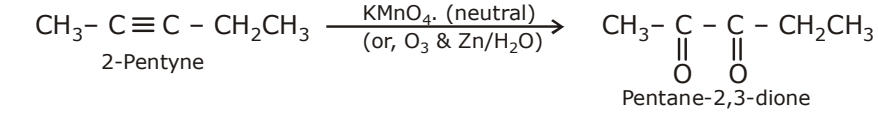
Q.11 Identify 'X' in the following reaction



(VIII) Oxidation of α-Dlketones

If an alkyne is treated with aqueous $KMnO_4$ under nearly neutral conditions, an α-diketone results.

General Reaction 

e.g. 

Ex.16 Give the product of the following reactions.

$H_3C - H_2C - C \equiv C - CH_2CH_2CH_3 \xrightarrow[Neutral]{KMnO_4} X$

$H_3C - H_2C - C \equiv C - CH_2CH_2CH_3 \xrightarrow[acidic\ higher\ temp]{KMnO_4} Y$

Sol. $X = CH_3CH_2\overset{\overset{O}{\|}}{C} - \overset{\overset{O}{\|}}{C}CH_2CH_2CH_3$ (α diketone)

$Y = CH_3CH_2COOH + HOOCCH_2CH_2CH_3$

(IX) Oxidative Cleavage

If the reaction mixture becomes warm or too basic the diketone undergoes oxidative cleavage. The products are the salts of carboxylic acids, which can be converted to the free acids by adding dilute acid.

General Reaction $R-C\equiv C-R' \xrightarrow[(\text{or } O_3, \text{ then } H_2O)]{\substack{(1)\ KMnO_4,\ ^-OH \\ (2)\ H^+}} R-\overset{O}{\overset{\|}{C}}-OH + HO-\overset{O}{\overset{\|}{C}}-R'$

e.g. $CH_3-C\equiv C-CH_2CH_3 \xrightarrow[(2)\ H^+]{(1)\ KMnO_4,\ NaOH} CH_3-\overset{O}{\overset{\|}{C}}-OH + HO-\overset{O}{\overset{\|}{C}}-CH_2CH_3$

e.g. $CH_3CH_2CH_2-C\equiv CH \xrightarrow[(2)\ H^+]{(1)\ KMnO_4,\ NaOH} CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}-OH + CO_2\uparrow$

Ex.17 Give the products of the following reactions

(i) $(CH_3)_2CHC\equiv CCH_2CH_2CH_3 \xrightarrow[\Delta]{KMnO_4} X$

(ii) $CH_3CH_2C\equiv CCH_2CH_3 \xrightarrow[\Delta]{KMnO_4} Y$

(iii) $HC\equiv CCH_2CH_2CH_3 \xrightarrow[\Delta]{KMnO_4} Z$

(iv) $CH_3C\equiv CCH_2CH_2C\equiv CCH_2CH_3 \xrightarrow[\Delta]{KMnO_4} W$

Sol. X: $(CH_3)_2CHCOOH + HOOCCH_2CH_2CH_3$

Y: $2CH_3CH_2COOH$, symmetrical internal alkynes give one acid

Z: $CH_3COOH + HOOCCH_2CH_2COOH + HOOCCH_2CH_3$

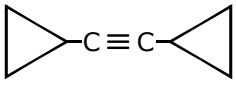
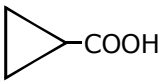
Q.12 C_5H_8 on $KMnO_4$ oxidation gives CO_2 and isobutyric acid. Identify C_5H_8.

(X) Ozonolysis

General reaction $R-C\equiv C-R' \xrightarrow[(ii)\ H_2O]{(i)\ O_3} R-COOH + R'-COOH$

e.g. $CH_3-C\equiv C-CH_2CH_3 \xrightarrow[(ii)\ H_2O]{(i)\ O_3} CH_3-COOH + CH_3CH_2-COOH$

Ex.18 C_8H_{10} (A) $\xrightarrow{O_3.H_2O}$ Acid (B) Identify (A) and (B) in the above reaction

Sol. (A)  (B) 

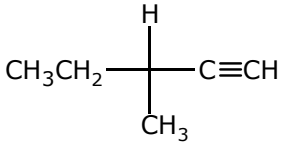
Ex.19 A certain hydrocarbon has the formula $C_{16}H_{26}$. Ozonation followed by hydrolysis gave $CH_3(CH_2)_4CO_2H$ and succinic acid as the only product. What is hydrocarbon

Sol. DU = 4

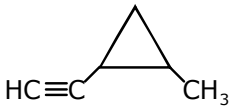
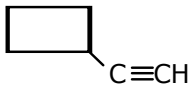
Hydrocarbon $C_{16}H_{26}$ is $CH_3(CH_2)_4\equiv CCH_2CH_2C\equiv C(CH_2)_4CH_3$

Solution Unsolved problems

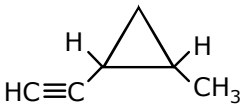
1. It means there is chiral carbon, hence structure is



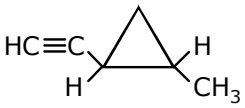
2. Alkyne (–C ≡ C–) has unsaturation hence C_5H_8 has also one ring of three or four carbon atoms.

(a)  (b) 

(a) Exists as cis-and trans-isomer



(cis)



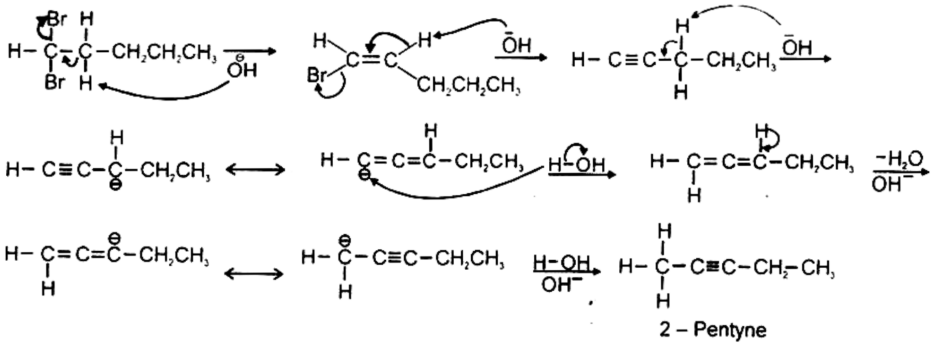
(trans)

3. $(\equiv C - H) < (= \underset{|}{C} - H) < (- \underset{|}{\overset{|}{C}} - H)$

Hence $\alpha < \beta < \gamma$

4. As the S-character of the orbital that binds carbon to another atom increases, the pair of electrons in that orbital is more strongly held and it requires more energy for homolytic cleavage of both the C – H and C – C bonds.

5. Mech.



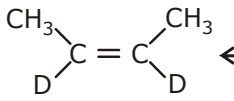
6. We need to add two groups to acetylene and ethyl group and a six-carbon aldehyde (to form the secondary alcohol). If we formed the alcohol group first, the weakly acidic – OH group would interfere with the alkylation by the ethyl group. Therefore, we should add the less reactive ethyl group first, and add the alcohol group later in the synthesis.

$$H - C \equiv C - H \xrightarrow[(ii)\ CH_3CH_2Br]{(i)\ NaNH_2} H - C \equiv C - CH_2CH_3$$

The ethyl group is not acidic and it does not interefere with the addition of the second group

$$H - C \equiv C - CH_2CH_3 \xrightarrow{NaNH_2} \overset{\oplus}{Na}\ \overset{\ominus}{C} \equiv C - CH_2CH_3$$

Reason : Electron donating groups such as R's make the π-bond more electron - rich and more reactive. Conversely, electron - withdrawing groups such as halogens make the π-bond more electron-poor and less reactive.

7. $CH_3 - C \equiv C - CH_3 \xrightarrow{D_2/Lindlar's\ catalyst}$  $\xleftarrow[CH_3COOD]{BD_3} CH_3 - C \equiv C - CH_3$

REACTION CHART FOR ALKANES

GMP

(1) $R-C\equiv CH \xrightarrow[200-300^\circ C]{H_2, Ni}$

or

$R-CH=CH_2$ Sabatier senderens reaction

(2) $R-X \xrightarrow[Red\,P-Hi,\,LiAlH_4]{Zn-Cu+HCl}$

(3) $R-Mg-X \xrightarrow[or\ NH_3\ or\ RNH_2]{+HOH\ or\ ROH}$

(4) $RX \xrightarrow[Wurtz\ reaction]{Na,\ dry\ ether}$

(5) $R-\underset{\underset{O}{\|}}{C}-Cl$ or ROH $\xrightarrow{Red\,P/HI}$

or

$R-\underset{\underset{O}{\|}}{C}-R$ or RCHO

(6) $R-\underset{\underset{O}{\|}}{C}-R \xrightarrow[Clemension's\ reduction]{Zn-Hg/Conc.\ HCl}$

(7) $R-\underset{\underset{O}{\|}}{C}-R \xrightarrow[Wolf/Kishner\ reduction]{H_2N-NH_2, HO^-, \Delta}$

or

$(RCH_2CH_2)_3B \xrightarrow{+H_2O}$

(8) $RCOONa \xrightarrow{NaOH+CaO}$

(9) $RCOONa \xrightarrow{Kolbe's\ electrolytic\ synthesis}$

R–H
or
R–R
or
C_nH_{2n+2}

(1) $\xrightarrow{X_2, h\nu\ or\ UV\ light\ or\ 400^\circ C} RX$

(2) $SO_2 + Cl_2 \xrightarrow[h\nu]{Reed\ reaction} RSO_2Cl$

(3) $\xrightarrow[Isomerisation]{AlCl_3/HCl}$ branched alkanes

(4) $\xrightarrow[500-700^\circ C]{Pyrolysis}$ Alkenes + CH_4 or C_2H_6

REACTION CHART FOR ALKENES

GMP

(1) $R-CH_2-CH_2-OH \xrightarrow[-H_2O]{conc.H_2SO_4}$

(2) $R-CH_2-CH_2-X \xrightarrow[-HX]{alc.KOH}$

(3) $R-CH_2-CH\langle^{X}_{X} \xrightarrow[\text{for higher alkene}\ -X_2]{Zn\ dust}$

(4) $R-\underset{X}{CH}-\underset{X}{CH_2} \xrightarrow{Zn\ dust}$

(5) $R-C\equiv CH \xrightarrow[200-300^\circ C]{Ni,\ H_2}$

(6) $\begin{matrix}RCH-COOK\\ |\\ RCH-COOK\end{matrix} \xrightarrow{Kolbe's\ electrolytic\ synthesis}$

(7) $(C_2H_5)_4N^+OH \xrightarrow{\Delta}$

(8) $R-\underset{\underset{O}{\|}}{C}-O-CH_2-CH_2-R \xrightarrow{Pyrolysis}$

$R-CH=CH_2$ or C_nH_{2n}

GR

(1) $\xrightarrow[200-300^\circ C]{H_2,\ Ni} R-CH_2-CH_3$

(2) $\xrightarrow{X_2} R-CHX-CH_2X$

(3) $\xrightarrow{HX} R-CHX-CH_3$

(4) $\xrightarrow{HBr,\ Peroxide} R-CH_2-CH_2Br$

(5) $\xrightarrow{HOCl} R-CH(OH)-CH_2Cl$

(6) $\xrightarrow[+H_2O]{dil.H_2SO_4} R-CH_2(OH)-CH_3$

(7) $\xrightarrow{BH_3} (RCH_2CH_2)_3B$

(8) $\xrightarrow[\Delta]{O_2} CO_2 + H_2O$

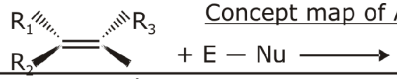
(9) $\xrightarrow{O_S\ O_4} R-\underset{OH}{CH}-\underset{OH}{CH_2}$

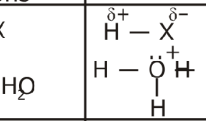
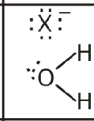
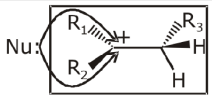
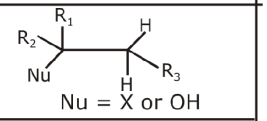
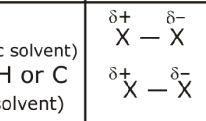
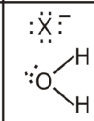
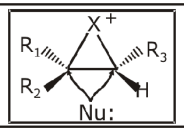
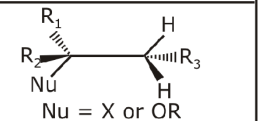
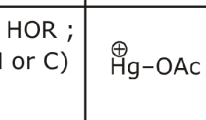
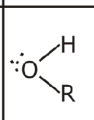
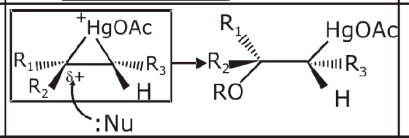
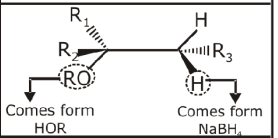
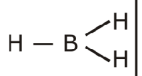
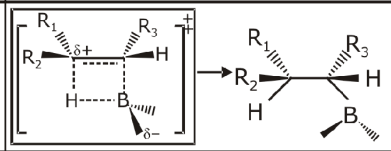
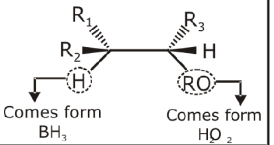
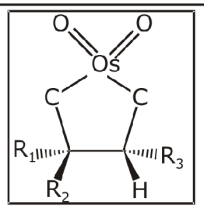
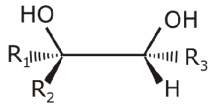
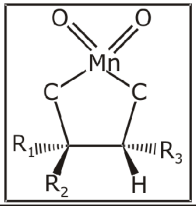
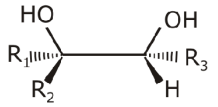
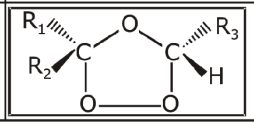
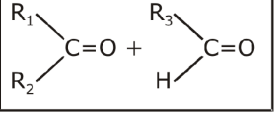
(10) $\xrightarrow[1\%\ alkaline\ KMnO_4]{Bayer\ reagent} R-\underset{OH}{CH}-\underset{OH}{CH_2}$

(11) $\xrightarrow[Ozonolysis]{O_3+H_2O} \begin{matrix}R\\ H\end{matrix}\!\!\diagdown\!\!C=O + O=C\!\!\diagup\!\!\begin{matrix}H\\ H\end{matrix}$

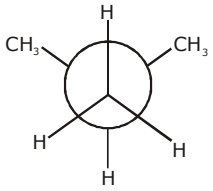
: 0744-2209671, 08003899588 | url : www.motioniitjee.com, :info@motioniitjee.com

Concept map of Alkene (Summery of Electrophillic addition Reaction of alkenes)



	Reaction Conditions	Electrophile	Nucleophile	Key Intermediates or Transition State	Regiochemistry	Stereochemistry of addition	Product
Hydrohalogenation Hydration(acid cat.)	H — X Cat. HA, H_2O				Markonikov Markonikov	Syn and anti	
Halogenation Halohydrin Formation	X_2 (non-nucleophillic solvent) X_2, ROH; R=H or C (nucleophillic solvent)				Not applicable Markonikov	Anti Anti	
Oxymercuration Demercuration (OMDM)	(1) $Hg(OAc)_2$, HOR ; THF (R=H or C) (2) $NaBH_4$				Markonikov	Syn and anti	
Hydroboration Oxidation (HBO)	(1) BH_3: THF (2) H_2O_2, ^-HO				Net anti-Markonikov	Syn	
1,2-Dihydroxylation	(1) OsO_4 (2) $NaHSO_4$					Syn	
Cold alkaline $KMnO_4$ (Baeyer's Reagent)	(1) MnO_4^- (2) H_2O					Syn	
Ozonolysis	(1) O_3 (2) Zn + H_2O / $(CH_3)_2S$	O_3				Syn addition	

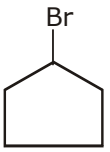
Exercise - I OBJECTIVE PROBLEMS (JEE MAIN)

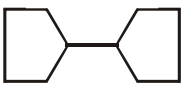
1.  $\xrightarrow{Br_2,hv}$ Major Product

(A) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2Br$ (B) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CBr}}-CH_3$

(C) $CH_3CH_2CH_2Br$ (D) $CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_3$

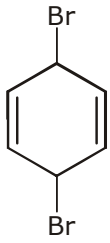
Sol.

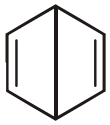
2.  $\xrightarrow[D.E]{Na}$ (A) Major product (A) is :

(A)  (B) 

(C)  (D) 

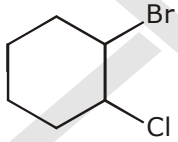
Sol.

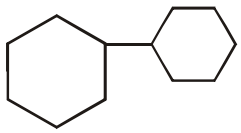
3.  $\xrightarrow[D.E]{Na}$ (A)

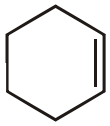
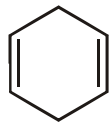
(A)  (B) 

(C)  (D) 

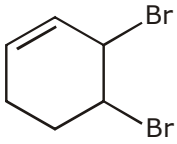
Sol.

4.  $\xrightarrow[D.E]{Na}$ (A)

(A)  (B) 

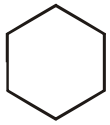
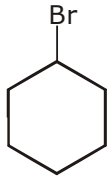
(C)  (D) 

Sol.

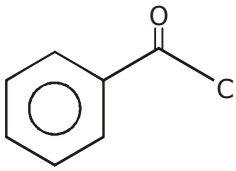
5.  $\xrightarrow[D.E]{Na}$ (A) $\xrightarrow[\Delta]{se}$ (B)

Product (B) will be :

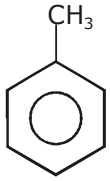
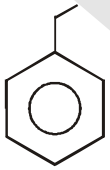
(A)  (B) 

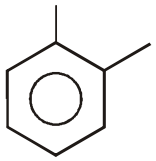
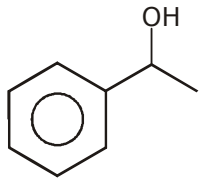
(C)  (D) 

Sol.

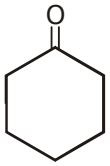
6.  $\xrightarrow[HCl]{Zn(Hg)}$ (A)

(Major) Product (A) will be :

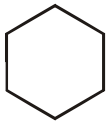
(A)  (B) 

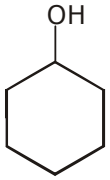
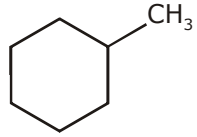
(C)  (D) 

Sol.

7.  $\xrightarrow[\Delta]{N_2H_4}$ (A) $\xrightarrow[\Delta]{KOH}$ (B)

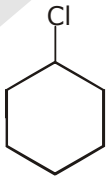
Product (B) will be :

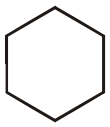
(A)  (B) 

(C)  (D) 

Sol.

8.  $\xrightarrow[h\nu]{Cl_2}$ (A). Product (A) will be :

(A)  (B) 

(C)  (D) 

Sol.

9. n-Pentane $\xrightarrow[hv]{Cl_2}$ (A)

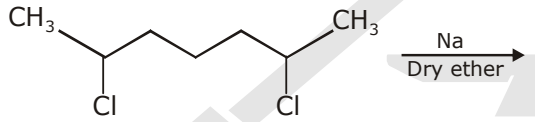
(A) 2 (B) 3
(C) 4 (D) 5

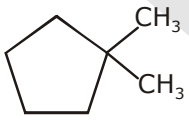
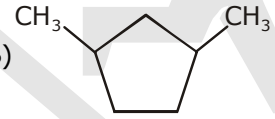
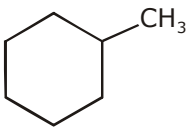
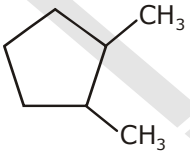
Sol.

10. $CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_2-CH_3 \xrightarrow[hv]{Cl_2}$

Mono-chloro product (inculding steroisomers) are :
(A) 6 (B) 7
(C) 8 (D) 9

Sol.

11. 

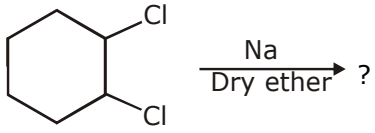
(A) 
(B) 
(C) 
(D) 

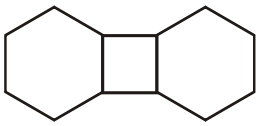
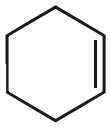
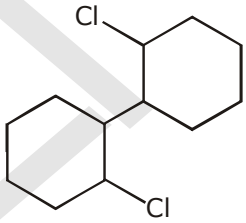
Sol.

12. $CH_3 - Cl + CH_3 - CH_2 - Cl \xrightarrow[\text{Dry ether}]{Na}$

products.
Which of the following is not the free radical combination product in wurtz process.
(A) $CH_3 - CH_3$
(B) $CH_3 - CH_2 - CH_3$
(C) $CH_3 - CH_2 - CH_2 - CH_3$ (D) CH_4

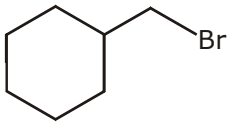
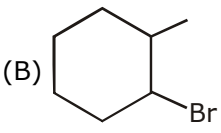
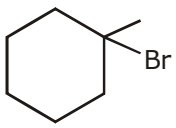
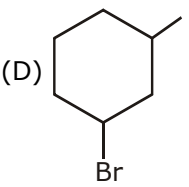
Sol.

13. 

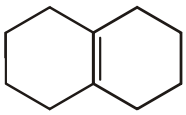
(A) 
(B) 
(C) 
(D) 

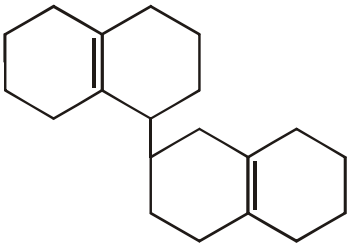
Sol.

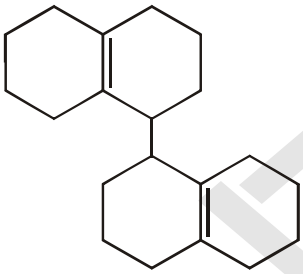
14. Methyl cyclohexane react with Br_2 in presence of u.v. light major product will be

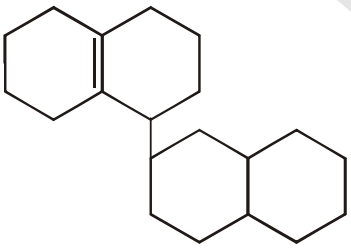
(A) 
(B) 
(C) 
(D) 

Sol.

15.  $\xrightarrow[h.v.]{Br_2}$ (A) $\xrightarrow[DMF]{Na}$ (B)(B) is

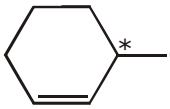
(A) 

(B) 

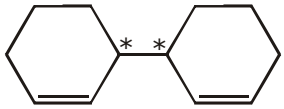
(C) 

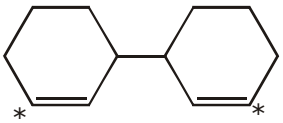
(D) None of these

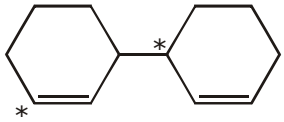
Sol.

16.  $\xrightarrow[\text{Dry ether}]{Na}$?

Possible prodcuts are :($C = C^{14}$)

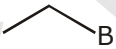
(A) 

(B) 

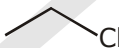
(C) 

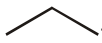
(D) All of these

Sol.

17. (i)  $\xrightarrow[D.E]{Na}$ 

(ii)  $\xrightarrow[D.E]{Na}$ 

(iii)  $\xrightarrow[D.E]{Na}$ 

(iv)  $\xrightarrow[D.E]{Na}$ 

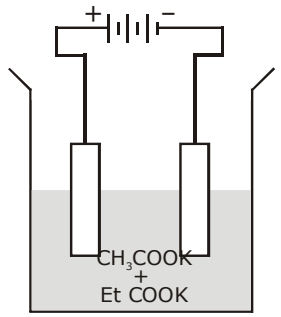
Correct order of rate of reaction will be

(A) iv > iii > i > ii (B) iii > iv > i > ii

(C) iv > i > iii > ii (D) None of these

Sol.

18.

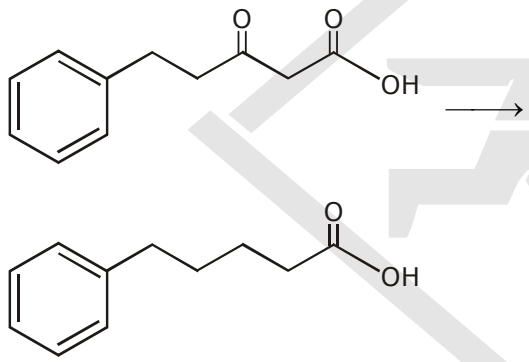


Which of the gases evolved on the surface of anode.

(A) C_2H_6, H_2
(B) C_3H_8, H_2
(C) $C_2H_6 + C_4H_6 + CO_2$
(D) $C_2H_6 + C_4H_{10} + CO_2 \uparrow$

Sol.

19.



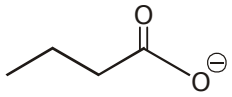
Suitable reagent for following cenversion will be :

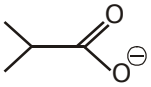
(A) Zn – Hg + HCl (B) Mg(Hg)
(C) H—Br (D) All of these

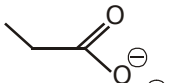
Sol.

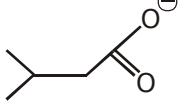
20. X $\xrightarrow{\text{electrolysis}}$ 2, 3-dimethyl butane

Which of the following anion will be migrates towards anode to prepare 2, 3-dimethyl butane in the given reaction.

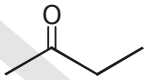
(A) 

(B) 

(C) 

(D) 

Sol.

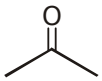
21. 

$\xrightarrow{NH_2NH_2+OH^-/\Delta}$ Most stable

confomer of product will be (across C_2 — C_3 bond) :

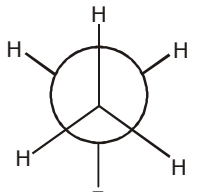
(A) gauche (B) Anti
(C) Eclipsed (D) Partially eclipsed

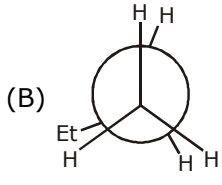
Sol.

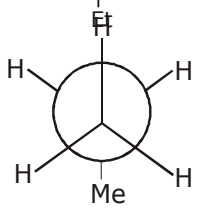
22. 

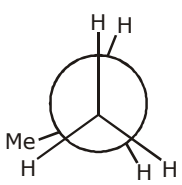
$\xrightarrow[\Delta]{Zn\text{-}Hg+HCl}$ most stable

confomer of product will be :

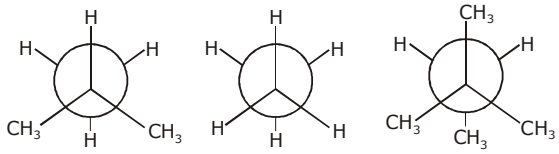
(A) 

(B) 

(C) 

(D) 

Sol.

23. 

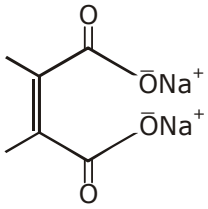
(I) (II) (III)

Correct order of mono bromination of given compound is :

(A) I > III > II (B) I > II > III (C) II > I > III

(D) III > II > I

Sol.

24.  Electrolysis → major product

will be

(A) 1-butyne (B) n-butane

(C) 2-butene (D) 2-butyne

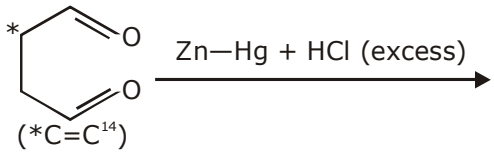
Sol.

25. In kolbe's electrolytic synthesis the pOH of solution will be

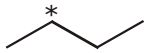
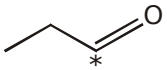
(A) decreases (B) Increases

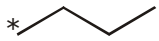
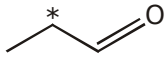
(C) Constant (D) None of these

Sol.

26. 

product will be :

(A)  (B) 

(C)  (D) 

Sol.

27. Rate of decarboxylation of following carboxylic acid with sodalime will be in order

$CH_3COOH \xrightarrow[r_1]{NaOH+CaO}$

$CH_3CH_2COOH \xrightarrow[r_2]{NaOH+CaO}$

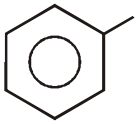
$CH_3-\underset{CH_3}{\underset{|}{CH}}-COOH \xrightarrow[r_3]{NaOH+CaO}$

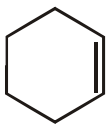
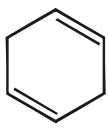
(A) $r_1 > r_2 > r_3$ (B) $r_3 > r_2 > r_1$

(C) $r_2 > r_3 > r_1$ (D) $r_1 > r_3 > r_2$

Sol.

28. Benzoic acid $\xrightarrow[NaOH+CaO]{\Delta}$ Product will be

(A)  (B) 

(C)  (D) 

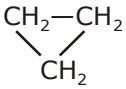
Sol.

29. Number of required O_2 mole for complete combustion of one mole of propane-
(A) 7 (B) 5
(C) 16 (D) 10

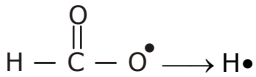
Sol.

30. How much volume of air will be needed for complete combustion of 10 lit. of ethane-
(A) 135 lit (B) 35 lit.
(C) 175 lit (D) 205 lit.

Sol.

31. $BrCH_2 — CH_2 — CH_2Br$ reacts with Na in the presence of ether at 100°C to produce -
(A) $BrCH_2 — CH = CH_2$
(B) $CH_2 = C = CH_2$
(C) 
(D) All of these

Sol.

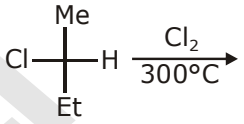
32. 
Driving force of above reaction is
(A) ΔH = — ve, ΔS = +ve
(B) ΔH = – ve, ΔS = –ve
(C) ΔH = +ve, ΔS = –ve
(D) ΔH = +ve, ΔS = +ve

Sol.

33. $e^{\ominus} + CH_3 — Cl \longrightarrow CH_3\bullet + Cl^{\ominus}$
Above reaction is a step of wurtz reaction electron will attack on which vacant orbital of methyl chloride.
(A) p-orbital
(B) anti-bonding orbital
(C) s-orbital
(D) d-orbital of chlorine

Sol.

34. Pick the correct statement for monochlorination of R-secbutyl chlorine.



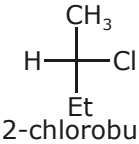
(A) There are four possible products ; three are optically active one is optically inactive
(B) There are five possible products ; three are optically inactive & two are optically active
(C) There are five possible products ; two are optically inactive & three are optically active
(D) There are four possible products ; two are optically active & two are optically inactive

Sol.

35. **Reaction :— 1** $CH_3—CH_2—CH_2—CH_2—CH_3$

$\xrightarrow[hv]{Cl_2}$ Optically active monochloro product (s) are (R)

Reaction :— 2



$\xrightarrow[hv]{Cl_2}$

S-2-chlorobutane

Optically active di-chloro product(s) are (S)

Reaction :— 3  $\xrightarrow[hv]{Cl_2}$ Optically active di-chloro product(s) are (P)

Reaction :— 4 2-methoxy propane

$\xrightarrow[hv]{Cl_2}$ Optically active mono chloro product(s) are (Q)

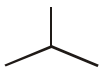
sum of P + Q + R + S is

(A) 8 (B) 9

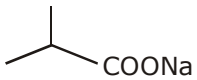
(C) 10 (D) 11

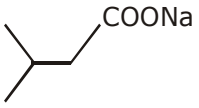
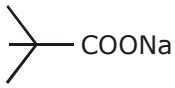
Sol.

Multiple Choice Questions :

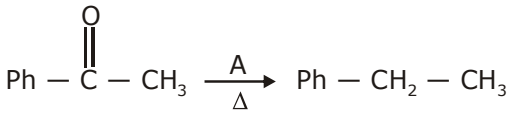
36. (X) $\xrightarrow[+\ CaO]{NaOH}$ 

(X) will be

(A)  (B) 

(C)  (D) 

Sol.

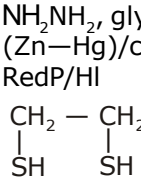
37. 

A could be :

(A) NH_2NH_2, glycol/OH^-

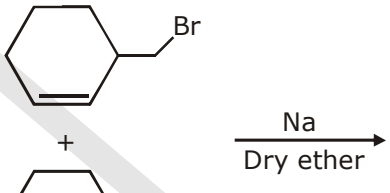
(B) (Zn—Hg)/conc. HCl

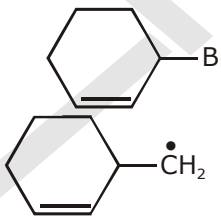
(C) RedP/HI

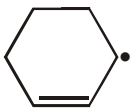
(D)  ; Raney Ni — H_2 (mozingo)

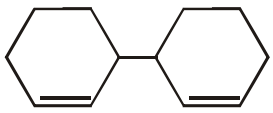
Sol.

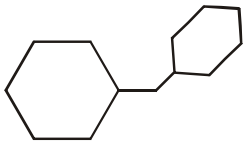
38. Which of the following is not produced as an intermediate during the reation :



(A) 

(B) 

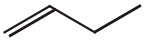
(C) 

(D) 

Sol.

39. Possible product during the reation will be :

$$2EtBr \xrightarrow[\text{Dry ether}]{Na}$$

(A)  (B) 

(C) $CH_3 - CH_3$ (D) 

Sol.

40. Which of the following acid salt does not give alkene as an major product when it is electroysed.
(A) Maleic acid (B) Oxalic acid
(C) Succinic acid (D) Adipic acid

Sol.

True or False :

41. Clemenson reduction is not useful for reduction of acid-sensitive compound

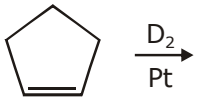
Sol.

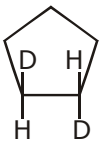
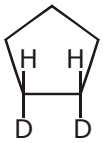
42. Wolf-kishner reduction is used for reduction of Base-sensitive compound.

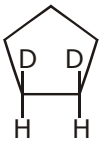
Sol.

Exercise - II JEE ADVANCED (Objective)

Single Choice Questions :

1.  Product will be :

(A)  (B) 

(C)  (D) B & C both

Sol.

2. Which of the following reagent not gives syn addition when react with alkyne.
(A) H_2 + Pd ($CaCO_3$ + Quinoline)
(B) P — 2 catalyst
(C) Raney Nickel (D) Li/liq. NH_3

Sol.

3. $CH_3 - C \equiv C - CH_3 \xrightarrow[Pd-BaSO_4]{H_2} (A)$

$\xrightarrow{\text{cold. } KMnO_4}$ (B). Compound (B) is :
(A) Meso (B) Recemic mixture
(C)Diastereomers (D) All

Sol.

4. Which of the following will decolourise alkaline $KMnO_4$ solution ?
(A) C_3H_8 (B) CH_4
(C) CCl_4 (D) C_2H_4

Sol.

5. $CH_3 - C \equiv C - CH_3 \xrightarrow[liq.\ NH_3]{Na} (A)$

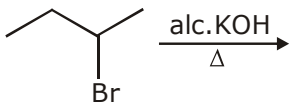
$\xrightarrow{\text{cold. } KMnO_4}$ (B)
(A) Meso (B) Racemic mixture
(C) Diastereomers (D) All

Sol.

6. $CH_3 - C \equiv C - CH_3 \xrightarrow[Pd-BaSO_4]{H_2} (A)$

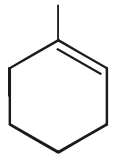
$\xrightarrow[CCl_4]{Br_2}$ (B)
(A) Meso (B) Racemic mixture
(C) Diastereomers (D) All

Sol.

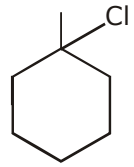
7. 

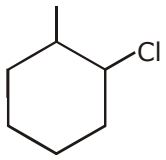
Total number of products.
(A) 2 (B) 3
(C) 4 (D) 5

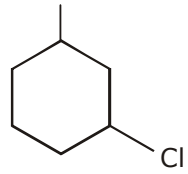
Sol.

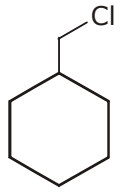
8.  $\xrightarrow[\text{Peroxide}]{HCl}$ (X) (Major product)

Structure of (X) will be

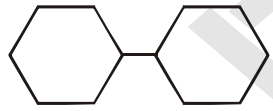
(A) 

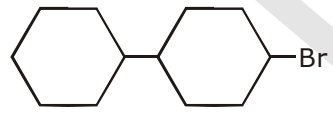
(B) 

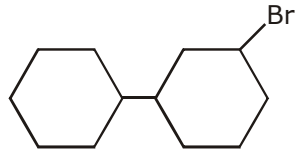
(C) 

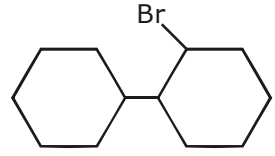
(D) 

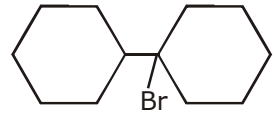
Sol.

9. Major product for the reaction  $\xrightarrow[h\nu]{Br_2}$ is :

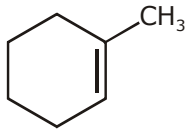
(A) 

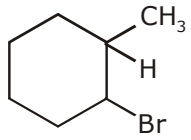
(B) 

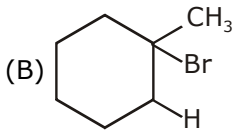
(C) 

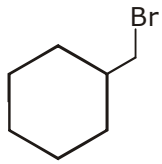
(D) 

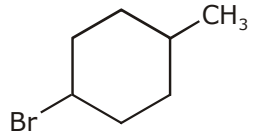
Sol.

10.  $\xrightarrow[\text{Peroxide}]{HBr}$ Major product will be :

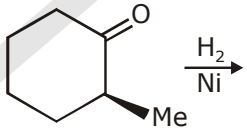
(A) 

(B) 

(C) 

(D) 

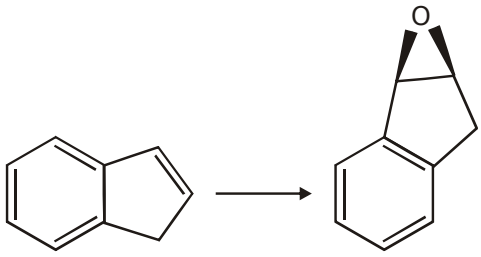
Sol.

11. 

Product of above reaction is
(A) Meso
(B) racemic
(C) Distereomers
(D) Optically inactive mixture

Sol.

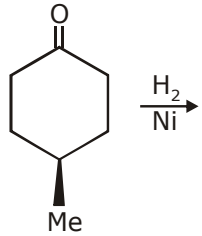
12. Suggest reagent and condition for the asymmetric synthesis of the epoxide given.



(A) $H_3O^{\oplus}$ (B) $H_2O/HO^{\ominus}$

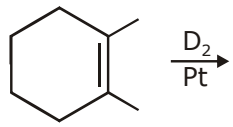
(C) CH_3CO_3H (D) $CH_3CO_2H/H^{\oplus}$

Sol.

13. 

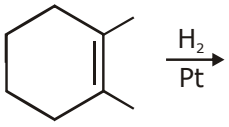
product of above reaction is
(A) Meso
(B) Racemic
(C) Diastereomers
(D) Optically active products.

Sol.

14. 

product of above reaction is
(A) Racemic (B) Diastereomers
(C) Enantiomer (D) None

Sol.

15. 

product of above reaction is
(A) Racemic (B) Diastereomers
(C) Enantiomer (D) Meso

Sol.

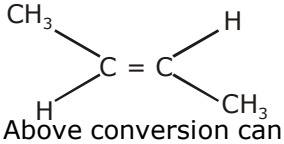
16. $CH_3 - C \equiv C - CH_2 - CH = CH - CH_2 - \overset{O}{\overset{\|}{C}} - Cl$
(a) (b) (c)
Reactivity toward catalytic hydrogenation
(A) a > b > c (B) b > a > c
(C) a > c > b (D) c > a > b

Sol.

17. $CH_3 - C \equiv C - CH_2 - CH = CH_2$
(a) (b)
Reactivity toward electrophilic addition reaction.
(A) a > b (B) b > a
(C) a = b (D) Cannot predict

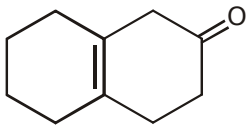
Sol.

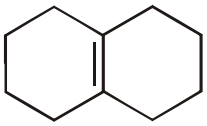
18. $CH_3 - C \equiv C - CH_3 \longrightarrow$

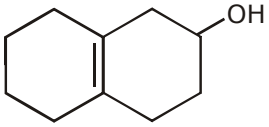


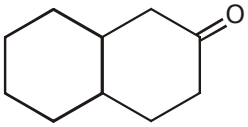
Above conversion can be acheived by
(A) Na/ liq NH_3 (B) Li / liqNH_3
(C) Li / EtOH (D) All

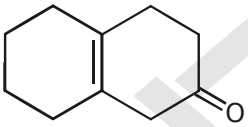
Sol.

19.  $\xrightarrow[Pd-C]{H_2}$ (A), Product (A) is

(A) 

(B) 

(C) 

(D) 

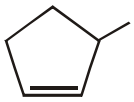
Sol.

20. Which of following will reacts with Na / liqNH_3 ?

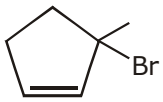
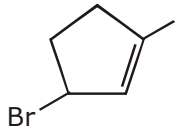
(A) 

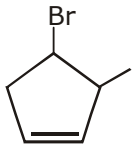
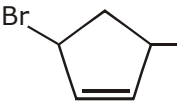
(B) $CH_3 - C \equiv C - CH_3$
(C) $CH_3 - C \equiv C - H$
(D) All

Sol.

21.  + Br_2 $\xrightarrow{hv}$ mixture of product.

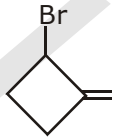
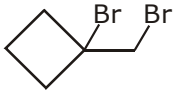
Among the following which product will formed minimum amount.

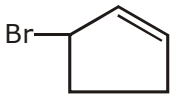
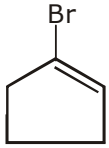
(A)  (B) 

(C)  (D) 

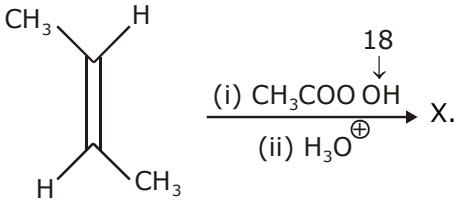
Sol.

22.  $\xrightarrow[\Delta]{H_2SO_4}$ P (Major) $\xrightarrow{NBS}$ Q (Major). The structure of Q is

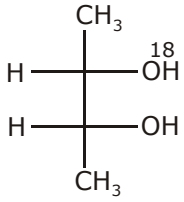
(A)  (B) 

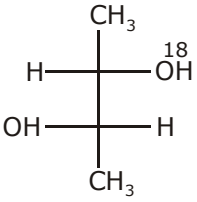
(C)  (D) 

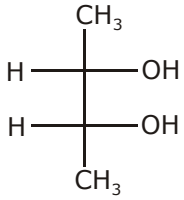
Sol.

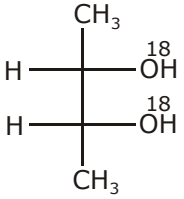
23. 

The probable structure of 'X' is

(A) 

(B) 

(C) 

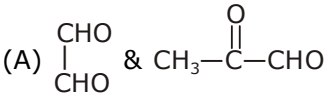
(D) 

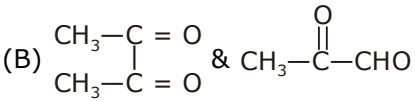
Sol.

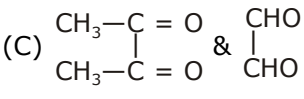
24. Ozonolysis of $CH_3—CH=C=CH_2$ will give
(A) Only CH_3CHO
(B) Only HCHO
(C) Only CO_2
(D) Mixture of CH_3CHO, HCHO & CO_2

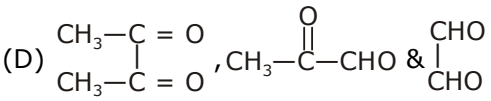
Sol.

25. O-xylene on ozonolysis will give

(A) 

(B) 

(C) 

(D) 

Sol.

26. 1-Penten-4-yne reacts with 1 mol bromine at -80°C to produce :
(A) 4, 4, 5, 5-Tetrabromopentene
(B) 1, 2-Dibromo-1, 4-pentadiene
(C) 1, 1, 2, 2, 4, 5-hexabromopentane
(D) 4, 5-dibromopentyne

Sol.

27. Anti—Markownikoff's addition of HBr is not observed in -
(A) Propene
(B) But-2-ene
(C) Butene
(D) 1-Methylcyclohexene

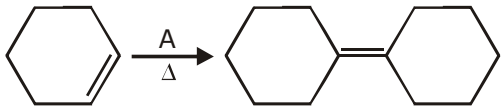
Sol.

28. Which alkene on heating with alkaline $KMnO_4$, Δ solution gives acetone and a gas, which turns lime water milky.
(A) 2-Methyl-2-butene
(B) isobutylene
(C) 1-Butene
(D) 2-Butene

Sol.

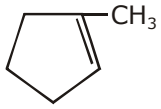
29. Which is expected to react most readily with bromine -
(A) $CH_3CH_2CH_3$ (B) $CH_2 = CH_2$
(C) $CH \equiv CH$ (D) $CH_3 — CH = CH_2$

Sol.

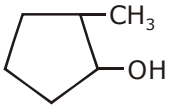
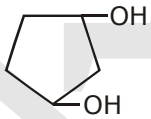
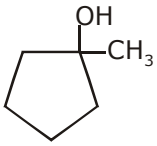
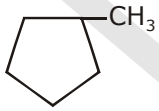
30. 

A can be –
(A) Conc. H_2SO_4 (B) alcoholic KOH
(C) Et_3N (D) t-BuOK

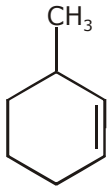
Sol.

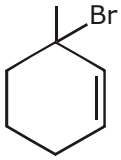
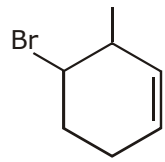
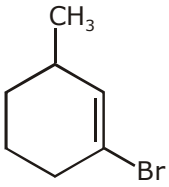
31. 

(i) $Hg(OAC)_2, H_2O$
(ii) $NaBH_4/NaOH/H_2O$ A.A is –

(A) 
(B) 
(C) 
(D) 

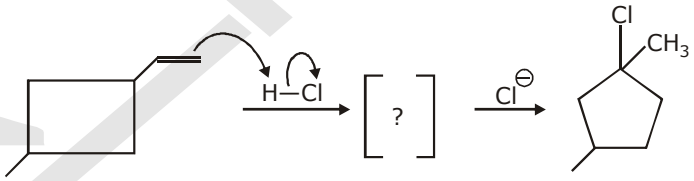
Sol.

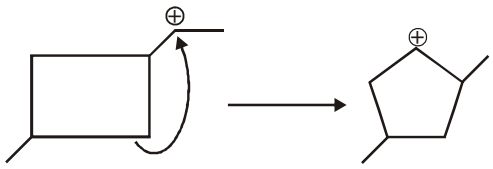
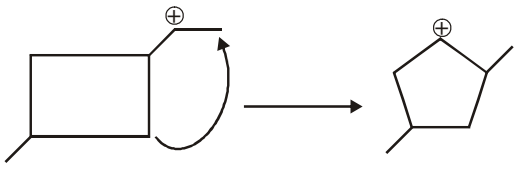
32.  NBS → Major product will be :

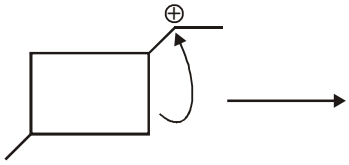
(A) 
(B) 
(C) 
(D) All

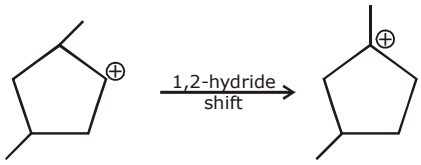
Sol.

33. Write mechanism best accounts for the transformation in the brackets ?

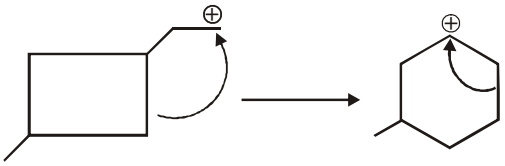


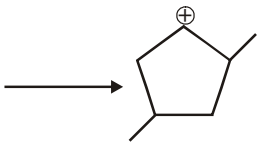
(A) 
(B) 
(C)





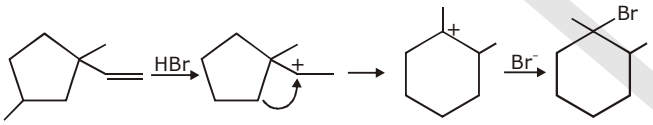
(D)



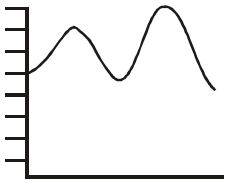


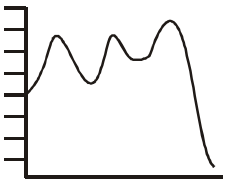
Sol.

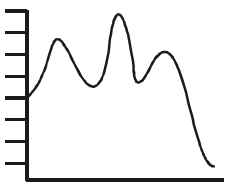
34. Consider the following rearrangement reaction:

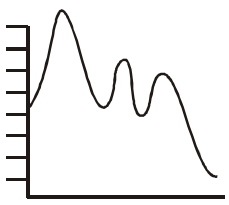


Which of the following reaction coordinates best represents the overall reaction ? (Note: the units are arbitrary)

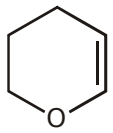
(A) 

(B) 

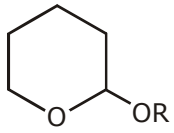
(C) 

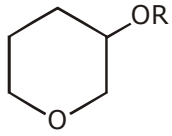
(D) 

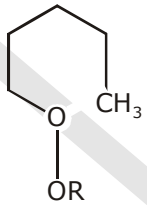
Sol.

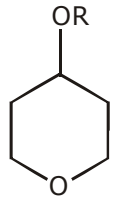
35.  $\xrightarrow{ROH/H^+}$ P (major)

The product P is

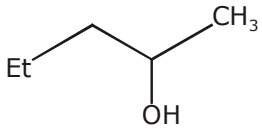
(A) 

(B) 

(C) 

(D) 

Sol.

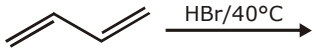
36.  $\xrightarrow[\Delta]{H^+}$ (P) major

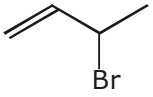
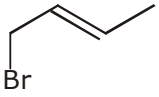
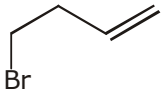
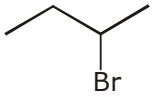
$\xrightarrow[CCl_4]{Br_2}$ Products

Products obtained at the end of the reaction are

(A) Meso compound
(B) Racemic mixture
(C) Diastereomeric mixture
(D) Structural isomers

Sol.

37. 
Thermodynamically controlled product will be :

(A) 
(B) 
(C) 
(D) 

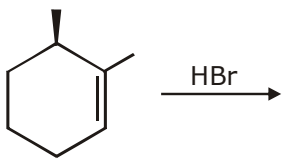
Sol.

38. (A) $C_4H_{10}O \xrightarrow[\Delta]{\text{Conc. } H_2SO_4} CH_3 - \overset{CH_3}{\overset{|}{C}} = CH_2 \xrightarrow{\text{dil.}H_2SO_4} (B)\ C_4H_{10}O$

What is relationship between A & B ?
(A) A and B may be position isomer (B) A and B may be chain isomers
(C) A and B may be stereoisomers
(D) All of the above

Sol.

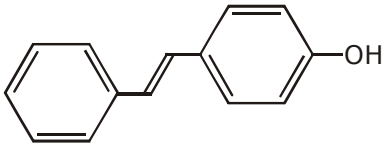
39. The product(s) of the following reaction can best be described as :

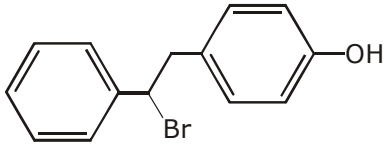
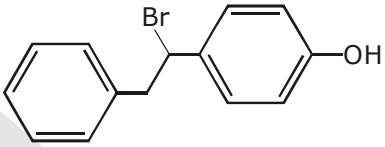
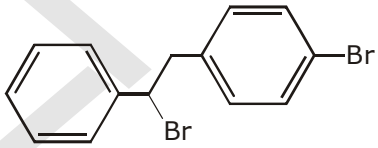
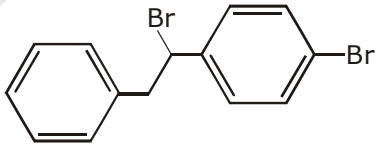


(A) A racemic mixture
(B) A single enantiomer
(C) A pair of diasteromers
(D) An achiral molecule

Sol.

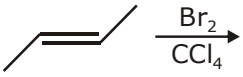
40. The reaction of HBr with the following compound would produce :



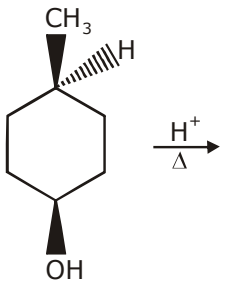
(A) 
(B) 
(C) 
(D) 

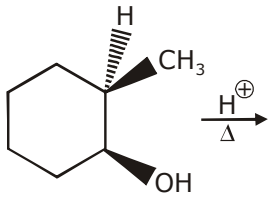
Sol.

41. In which of the following reaction formation of racemic mixture.

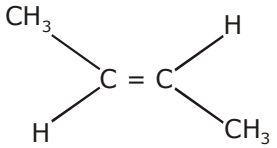
(A)  $\xrightarrow[CCl_4]{Br_2}$

(B)  $\xrightarrow{Cold,\ KMnO_4}$

(C) 

(D) 

Sol.

42.  $\xrightarrow[CCl_4]{Br_2}$ (X) Products. Value of x is

(A) 4 (B) 1
(C) 2 (D) 3

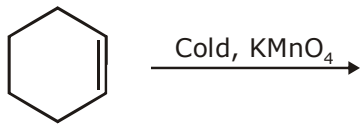
Sol.

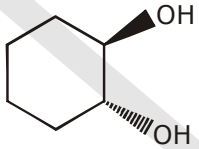
43.  $\xrightarrow[CCl_4]{Br_2}$ Products obtained in this reaction are

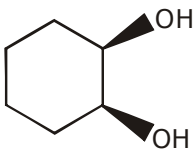
(A) Diastereoismers
(B) Enantiomers
(C) Positional isomers
(D) Single meso compound

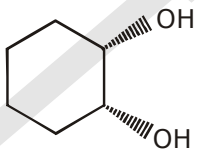
Sol.

44. In the given reaction :



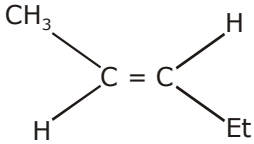
(A) 

(B) 

(C) 

(D) B and C both

Sol.

45.  $\xrightarrow[CCl_4]{Br_2}$ P; 'P' is :

(A) Racemic mixture
(B) Diastereomer
(C) Mixture of Threo compounds
(D) Meso compound

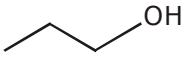
Sol.

46. $CH_3 - CH = CH_2 \xrightarrow{dil.H_2SO_4}$ (A) .
Product (A) is

(A) 

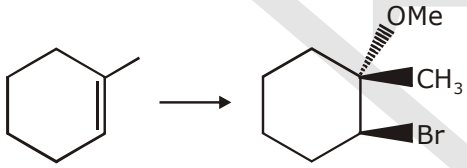
(B) $CH_3 - CH_2 - CH_2 - OSO_2OH$

(C) $CH_3 - \underset{\underset{O - SO_2OH}{|}}{CH} - CH_3$

(D) 

Sol.

47. Which reaction condition would be perform the following transformations ?



(A) HOBr, $CH_3OH/H^{\oplus}$
(B) OsO_4, HBr, NaOH, MeI
(C) Br_2\ MeONa
(D) mCPBA, HBr, NaOH, MeI

Sol.

48. $Me - \underset{\underset{Et}{|}}{CH} - CH = CH - Ph \xrightarrow{HCl}$ W, W is

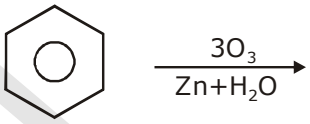
(A) $Me - \underset{\underset{Et}{|}}{CH} - CH_2 - \underset{\underset{Cl}{|}}{CH} - Ph$

(B) $Me - \underset{\underset{Et}{|}}{CH} - \underset{\underset{Cl}{|}}{CH} - CH_2 - Ph$

(C) $Me - \underset{\underset{Cl}{|}}{CH} - \underset{\underset{Et}{|}}{CH} - \underset{\underset{Ph}{|}}{CH_2}$

(D) $Cl - \underset{\underset{Et}{|}}{CH} - \underset{\underset{Me}{|}}{CH} - CH_2 - Ph$

Sol.

49. 

Products are

(A) $\underset{\underset{CHO}{|}}{CO_2H}$

(B) $\underset{\underset{CO_2H}{|}}{CO_2H}$

(C) $\underset{\underset{CHO}{|}}{CHO}$

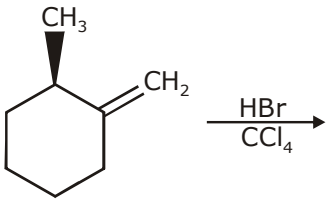
(D) $\underset{\underset{CH_2-CH_2-OH}{|}}{CH_2OH}$

Sol.

50. Gases libreated at the surface of anode and cathode respectively in kolbe's electrolytic syntheis will be :

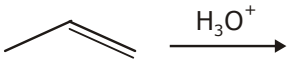
(A) H_2, CO_2 (B) CO_2, H_2
(C) NaOH, H_2 (D) Only CO_2

Sol.

51. 

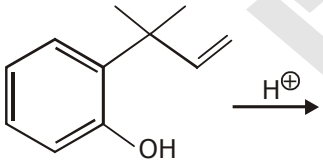
What is sterochemistry of products
(A) Optically inactive (B) Meso product
(C) Diastereomers (D) None of these

Sol.

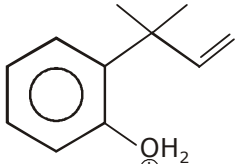
52. 

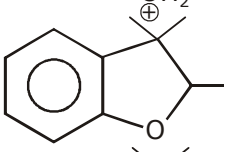
Shape of intermediate produced during this reaction will be
(A) Square planer (B) tetrahedral
(C) Trigonal planer (D) Pyramidical

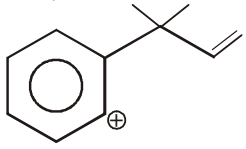
Sol.

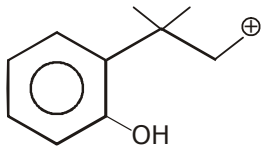
53. 

Which of the following is formed as an product during the following reaction

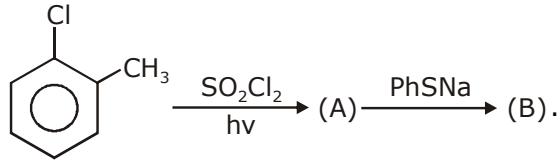
(A) 

(B) 

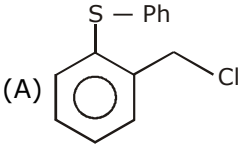
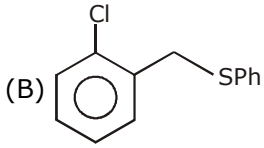
(C) 

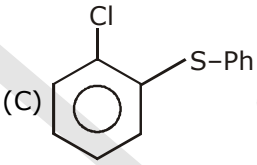
(D) 

Sol.

54. 

Product (B) is

(A)  (B) 

(C)  (D) None

Sol.

EXERCISE – III JEE ADVANCED

Single Choice Questions :

1. $CH_3 - C \equiv C - H \longrightarrow CH_3 - C \equiv C - CH_3$
Above conversion can be achieved by
(A) $NaNH_2$, $CH_3 - I$ (B) NaH, $CH_3 - I$
(C) Na, $CH_3 - I$ (D) All

Sol.

2. Which of the following is most reactive toward catalytic hydrogenation ?

(A) $R - \overset{\overset{O}{\|}}{C} - Cl$ (B) $R - C \equiv C - R$

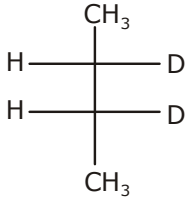
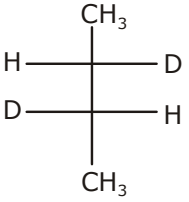
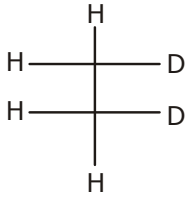
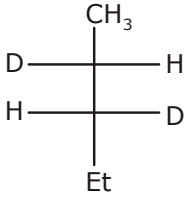
(C) $R - CH = CH - R$ (D) 

Sol.

3. Which of the following is least reactive toward hydrogenation ?
(A) $CH_3 - C \equiv C - CH_3$
(B) $CH_3 - C \equiv CH$
(C) $HC \equiv CH$
(D) $H_2C = CH_2$

Sol.

4. $CH_3 - C \equiv C - CH_3 \xrightarrow[Pd\text{-}BaSO_4]{H_2}$ (A) $\xrightarrow[Ni]{D_2}$ (B)
Product (B) of above reaction is

(A) 
(B) 
(C) 
(D) 

Sol.

5. $Ph - C \equiv C - Ph \xrightarrow[Liq.\ NH_3]{Na}$ (A) $\xrightarrow[Pt]{D_2}$ (B) Product (B) is
(A) Racemic (B) Diastereomer
(C) Enantiomer (D) None

Sol.

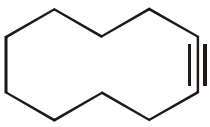
6. $C_3H_7C \equiv CH \xrightarrow[(1eq.)]{HBr}$ 'X' X is
(A) $C_3H_7CH = CHBr$ (B) $C_3H_7Br = CH_2$
(C) $C_3H_7CBr = \underset{\underset{H}{|}}{C} - Br$ (D) $C_3H_7HC = CBr_2$

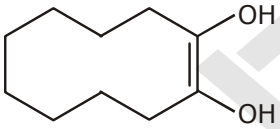
Sol.

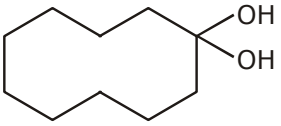
7. $CH_3 - C \equiv C - CH_3 \xrightarrow[(2)\ Br_2]{(1)\ H_2/Pt} X$

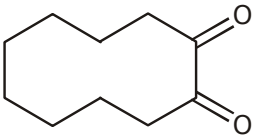
(A) (d)-2, 3-Dibromobutane
(B) (l)-2, 3-Dibromobutane
(C) (dl)-2, 3-Dibromobutane
(D) meso-2, 3-Dibromobutane

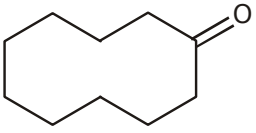
Sol.

8.  $\xrightarrow[H_2SO_4]{HgSO_4}$ P, Products P is

(A) 

(B) 

(C) 

(D) 

Sol.

9. $CH_3 - C \equiv CH \xrightarrow[H_2SO_4]{HgSO_4} (A)$;

$CH_3 - C \equiv C - CH_3 \xrightarrow[H_2SO_4]{HgSO_4} (B)$

Relation between (A) and (B)
(A) Position isomer
(B) Functional isomers
(C) Homologous
(D) Metamers

Sol.

10. $B \xleftarrow[Catalyst]{Lindlar} R - C \equiv C - R$

$\xrightarrow{Na/NH_3} A$

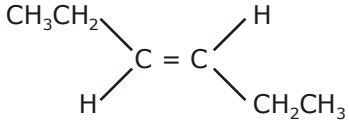
A and B are geometrical isomers (R – CH = CH – R) –
(A) A is trans, B is cis
(B) A and B both are cis
(C) A and B both are trans
(D) A is cis, B is trans

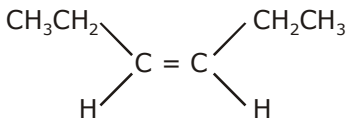
Sol.

11. $CH_3CH_2C \equiv CH \xrightarrow{NaNH_2/NH_3(liq.)}$

$\xrightarrow{CH_3CH_2Br}$ $\xrightarrow{Li,\ NH_3(liq.)}$

(A) $CH_3CH_2CH = CHCH_3$
(B) $CH_3CH_2CH = CH_2$

(C) 

(D) 

Sol.

12. **List I**

(A) $CH_3 - C \equiv C - CH_3 \longrightarrow$ cis-2-butene

(B) $CH_3 - C \equiv C - CH_3 \longrightarrow$ trans-2-butene

(C) $CH_3C \equiv C - CH_3 \longrightarrow$ 1-Butyne

(D) $CH_3 - CH_3 - C \equiv CH_3 \longrightarrow$ 2-Butyne

List II

(1) $Na/NH_3(\ell)$
(2) $H_2/Pd/BaSO_4$
(3) alc. KOH, Δ
(4) $NaNH_2$, Δ

Code :

	a	b	c	d
(A)	2	1	3	4
(B)	1	2	4	3
(C)	1	2	3	4
(D)	2	1	4	3

13. 

Product will be

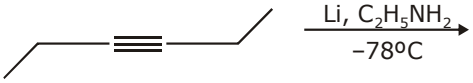
(A) 

(B) 

(C) 

(D) B and C both

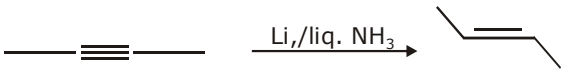
Sol.

14. 

Major product will be

(A) Z-3-Hexene (B) E-3 Hexene
(C) E-2-Hexene (D) A and B both

Sol.

15. 

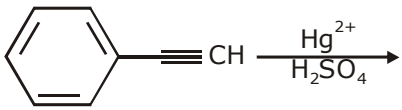
Major product

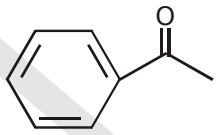
given reaction is an example of

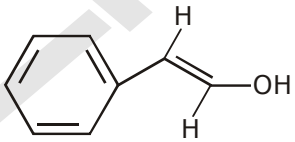
(A) catalytic hydrogenation
(B) Metal dissolved reduction
(C) Metal adsorbed reduction
(D) Non metal dissolved reduction

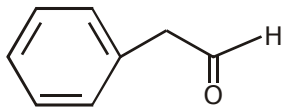
Sol.

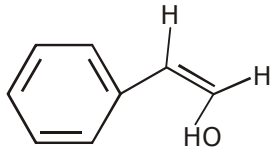
16. What is the major organic product of the following reaction ?



(A) 

(B) 

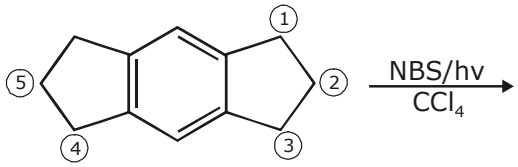
(C) 

(D) 

Sol.

Multiple Choice Questions :

17. Bromination can take place at



(A) 1 (B) 2
(C) 3 (D) 4

Sol.

18. Benzyl chloride ($C_6H_5CH_2Cl$) can be prepared from toluene by chlorination with :
(A) SO_2Cl_2 (B) $SOCl_2$
(C) Cl_2/hv (D) NaOCl

Sol.

19. An alkene on ozonolysis yields only ethanal. There are an structural isomers of this which on ozonolysis yields :
(A) propanone (B) ethanal
(C) methanal (D) only propanal

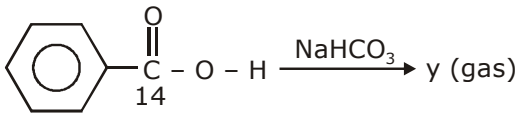
Sol.

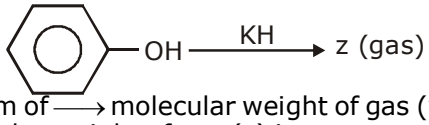
20. $CH_2 = CHCH_2CH = CH_2 \xrightarrow{NBS}$ possible products can be
(A) $CH_2 = CHCHCH = CH_2$ (Br)
(B) $CH_2 = CHCH = CH - CH_2Br$
(C) $CH_2 = CH\,CH_2\,CH = CHBr$
(D) $CH_2 = CHCH_2C = CH_2$ (Br)

Sol.

21. Which of the following will same product with HBr in presence or absence of peroxide
(A) Cyclohexene
(B) 1-methylcyclohexene
(C) 1,2-dimethylcyclohexene
(D) 1-butene

Sol.

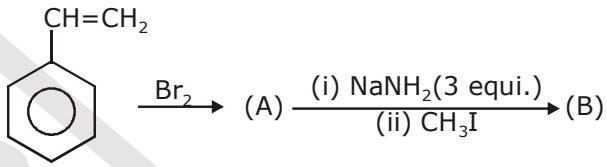
22. (i) 

(ii) 

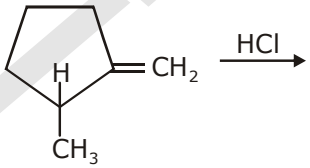
Sum of $\longrightarrow$ molecular weight of gas (y) + molecular weight of gas (z) is

Sol.

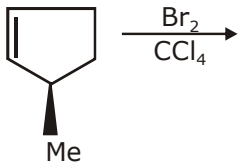
23. Complete the following reaction with appropriate sturcture of products/reagents



Sol.

24. (a) 

Total number of Markownikoff's products in above reaction is ?

(b) 

Number of products obtained in the above reaction is ?

(c) 

Total number of products obtgained in this reaction is ?

Sol.

EXERCISE – IV PREVIOUS YEARS PROBLEMS

LEVEL – I JEE MAIN

Q.1 The compound

$H_3C–\underset{\displaystyle H_3C}{\overset{|}{C}} = CH – CH_2 – CH_3 \xrightarrow{\text{Vigorous oxidation}}$ product, here product is **[AIEEE-2002]**

(A) CH_3COOH & $CH_3–\overset{\displaystyle O}{\overset{||}{C}}– CH_3$

(B) $CH_3 – CH_2 – COOH$ & $CH_3–\underset{\displaystyle CH_3}{\overset{|}{C}}=O$

(C) $CH_3 – CH_2 – COOH$ only

(D) HCOOH & $CH_3–\overset{\displaystyle O}{\overset{||}{C}}=CH_3$

Sol.

Q.2 Reaction

$H–C\equiv C–H + HOCl \longrightarrow$ product, here product will be - **[AIEEE-2002]**

(A) $CHCl_2–CHO$ (B) CHO–CHO

(C) CH–Cl=CHCl (D) $CHCl_2–CHCl_2$

Sol.

Q.3 Acetylene does not react with - **[AIEEE-2002]**

(A) $NaNH_2$ (B) NaOH

(C) Na metal (D) Ammonical $AgNO_3$

Sol.

Q.4 On mixing a certain alkane with chlorine and irradiating it with ultraviolet light, it forms only one monochloroalkane. This alkane could be - **[AIEEE-2003]**

(A) Isopentane (B) Neopentane

(C) Propane (D) Pentane

Sol.

Q. 5 Butene-1 may be converted to butane by reaction with – **[AIEEE-2003]**

(A) Zn – Hg (B) Pd / H_2

(C) Zn – HCl (D) Sn – HCl

Sol.

Q.6 During dehydration of alcohols to alkenes by heating with conc. H_2SO_4 the initiation step is- **[AIEEE-2003]**

(A) Elimination of water

(B) Formation of an easter

(C) Protonation of alcohol molecule

(D) Formation of carbocation

Sol.

Q.7 Bottles containing C_6H_5I and $C_6H_5CH_2I$ lost their original labels. They were labelled A and B for testing. A and B were separately taken in test tubes and boiled with NaOH solution. The end solution in each tube was made acidic with dilute HNO_3 and then some $AgNO_3$ solution was added. Substance B gave a yellow precipitate. Which one of the following statements is true for this experiment ? **[AIEEE-2003]**

(A) B was C_6H_5I

(B) Addition of HNO_3 was unnecessary

(C) A was C_6H_5I (D) A was $C_6H_5CH_2I$

Sol.

Q.8 Which one of the following has the minimum boiling point ? **[AIEEE-2004]**

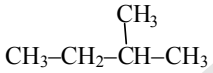
(A) n-Butane (B) 1-Butyne

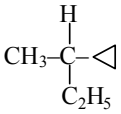
(C) 1-Butene (D) isobutane

Sol.

Q.9 Amongst the following compounds, the optically active alkane having lowest molecular mass is - **[AIEEE-2004]**

(A) $CH_3–CH_2–CH_2–CH_3$

(B) 

(C) 

(D) $CH_3–CH_2–C\equiv CH$

Sol.

Q.10 Reaction of one molecule of HBr with one molecule of 1,3–butadiene at 40ºC given predominantly **[AIEEE-2005]**

(A) 1–bromo–2–butene under thermodynamically controlled conditions

(B) 3–bromobutene under kinetically controlled conditions

(C) 1–bromo–2–butene under kinetically controlled conditions

(D) 3–bromobutene under thermodynamically controlled conditions

Sol.

Q.11 Acid catalyzed hydration of alkenes except ethene leads to the formation of – **[AIEEE-2005]**

(A) secondary or tertiary alcohol

(B) primary alcohol

(C) mixture of secondary and tertiary alcohols

(D) mixture of primary and secondary alcohols

Sol.

Q.12 Alkyl halides react with dialkyl copper reagents to give **[AIEEE-2005]**

(A) alkyl copper halides (B) alkenes

(C) alkenyl halides (D) alkanes

Sol.

Q.13 Elimination of bromine from 2–bromobutane results in the formation of – **[AIEEE-2005]**

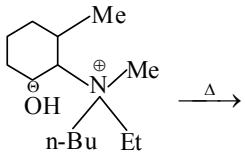
(A) predominantly 2–butene

(B) equimolar mixture of 1 and 2–butene

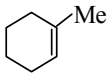
(C) predominantly 2–butyne

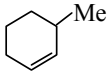
(D) predominantly 1–butene

Sol.

Q.14 

The alkene formed as a major product in the above elimination reaction is **[AIEEE 2006]**

(A) $CH_2 = CH_2$ (B) 

(C)  (D) 

Sol.

Q.15 Fluorobenzene (C_6H_5F) can be synthesized in the laboratory - **[AIEEE 2006]**

(A) from aniline by diazotisation followed by heating the diazonium salt with HBF_4

(B) by direct fluorination of benzene with F_2 gas

(C) by reacting bromobenzene with NaF solution

(D) by heating phenol with HF and KF

Sol.

Q.16 Phenyl magnesium bromide reacts with methanol to give - **[AIEEE 2006]**

(A) a mixture of benzene and Mg(OMe) Br

(B) a mixture of toluene and Mg(OH)Br

(C) a mixture of phenol and Mg(Me)Br

(D) a mixture of anisole and Mg(OH) Br

Sol.

Q.17 Which of the following reactions will yield 2, 2-dibromopropane? **[AIEEE 2007]**

(A) $CH_3 - C \equiv CH + 2HBr \rightarrow$

(B) $CH_3CH = CHBr + HBr \rightarrow$

(C) $CH \equiv CH + 2HBr \rightarrow$

(D) $CH_3 - CH = CH_2 + HBr \rightarrow$

Sol.

Q.18 In the following sequence of reactions, the alkene affords the compound 'B'

$CH_3CH = CHCH_3 \xrightarrow{O_3} A \xrightarrow[Zn]{H_2O} B$, The compound B is **[AIEEE 2008]**

(A) CH_3COCH_3

(B) $CH_3CH_2COCH_3$

(C) CH_3CHO

(D) CH_3CH_2CHO

Sol.

Q.19 The treatment of CH_3MgX with $CH_3C{\equiv}C{-}H$ produces **[AIEEE 2008]**

(A) $CH_3C{\equiv}C{-}CH_3$

(B) $CH_3 - \overset{H}{\underset{|}{C}} = \overset{H}{\underset{|}{C}} - CH_3$

(C) CH_4

(D) $CH_3{-}CH{=}CH_2$

Sol.

Q.20 The hydrocarbon which can react with sodium in liquid ammonia is - **[AIEEE 2008]**

(A) $CH_3CH_2C{\equiv}CH$

(B) $CH_3CH{=}CHCH_3$

(C) $CH_3CH_2C{\equiv}CCH_2CH_3$

(D) $CH_3CH_2CH_2C{\equiv}CCH_2CH_2CH_3$

Sol.

Q.21 Ozonolysis of an organic compounds gives formaldehyde as one of the products. This confirms the presence of : **[AIEEE 2011]**

(A) two ethylenic double bonds

(B) vinyl group

(C) an isopropyl group

(D) an acetylenic triple bond

Sol.

Q.22 Ozonolysis of an organic compound 'A' produces acetone and propionaldehyde in equimolar mixture. Identify 'A' from the following compounds : **[AIEEE 2011]**

(A) 1 - Pentene

(B) 2 - Pentene

(C) 2 - Methyl - 2 - pentene

(D) 2 - Methyl - 1 – pentene

Sol.

Q.23 2-Hexyne gives trans -2- Hexene on treatment with - **[AIEEE 2012]**

(A) Li/NH_3 (B) $Pd/BaSO_4$

(C) $LiAlH_4$ (D) Pt/H_2

Sol.

Q.24 Which branched chain isomer of the hydrocarbon with molecular mass 72u gives only one isomer of mono substituted alkyl halide ? **[AIEEE 2012]**

(A) Neopentane

(B) Isohexane

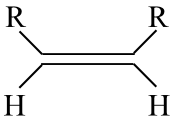
(C) Neohexane

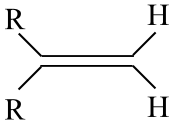
(D) Tertiary butyl chloride

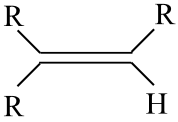
Sol.

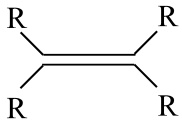
LEVEL – II JEE ADVANCED

Q.1 Which one of the following alkenes will react fastest with H_2 under catalytic hydrogenation condition– **[IIT '2000]**

(A) 

(B) 

(C) 

(D) 

Sol.

7

Q.2 Propyne and propene can be distinguished by – **[IIT '2000]**

(A) conc. H_2SO_4 (B) Br_2 in CCl_4

(C) dil. $KMnO_4$ (D) $AgNO_3$ in ammonia

Sol.

Q.3 **Statement-1 :** 1-butene on reaction with HBr in the presence of a peroxide produces 1-bromobutane.

Statement-2 : It involves the formation of a primary radical. **[IIT 2000]**

(A) Statement-1 is true, Statement-2 is true and statement-2 is correct explanation for statement-1

(B) Statement-1 is true, Statement-2 is true and statement-2 is NOT the correct explanation for statement-1

(C) Statement-1 is true, Statement-2 is false.

(D) Statement-1 is false, Statement-2 is true.

Sol.

Q.4 In the presence of peroxide, hydrogen chloride and hydrogen iodide do not give anti–Markonikoff addition to alkene because – **[IIT '2001]**

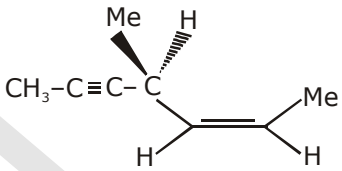
(A) both are highly ionic

(B) one is oxidising and the other is reducing

(C) one of the step is endothermic in both the cases

(D) All the steps are exothermic in both cases

Sol.

Q.5 

Hydrogenation of the above compound in the presence of poisoned paladium catalyst gives – **[IIT '2001]**

(A) An optically active compound

(B) An optically inactive compound

(C) A racemic mixture

(D) A diastereomeric mixture

Sol.

Q.6 The reaction of propene with HOCl proceeds via the addition of – **[IIT '2001]**

(A) H^+ in first step

(B) Cl^+ in first step

(C) OH^- in first step

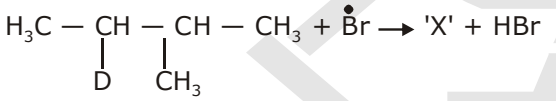
(D) Cl^+ and OH^- in single step

Sol.

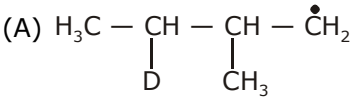
Q.7 **Statement-1 :** Addition of bromine to trans-2-butene yields meso-2, 3-dibromo butane.
Statement-2 : Bromine addition to an alkene is an electrophilic addition. **[IIT 2001]**
(A) Statement-1 is true, Statement-2 is true and statement-2 is correct explanation for statement-1 (B) Statement-1 is true, Statement-2 is true and statement-2 is NOT the correct explanation for statement-1
(C) Statement-1 is true, Statement-2 is false.
(D) Statement-1 is false, Statement-2 is true.

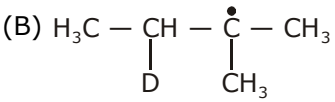
Sol.

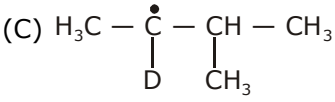
Q.8 Consider the following reactions – **[IIT '2002]**

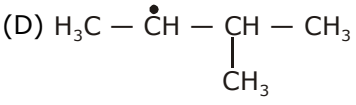


Identify the structure of the major product 'X'

(A) 

(B) 

(C) 

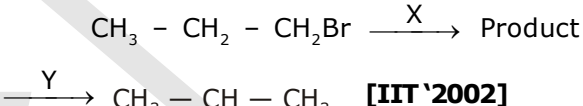
(D) 

Sol.

Q.9 Identify a reagent from the following list which can easily distinguish between 1–butyne and 2-butyne- **[IIT '2002]**
(A) bromine, CCl_4
(B) H_2, Lindlar catalyst
(C) dilute H_2SO_4, $HgSO_4$
(D) ammonical Cu_2Cl_2 solution

Sol.

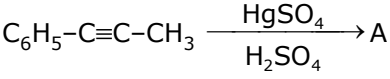
Q.10 Identify the set of reagents/reaction conditions 'X' and 'Y' in the following set of transformation



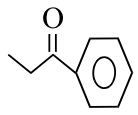
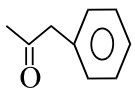
[IIT '2002]

(A) X = dilute aqueous NaOH, 20°C; Y = HBr/ acetic acid, 20°C
(B) X = concentrated alcoholic NaOH, 80°C; Y = HBr/acetic acid, 20°C
(C) X = dilute aqueous NaOH, 20°C; Y = Br_2/ $CHCl_3$, 0°C
(D) X = concentrated alcoholic NaOH, 80°C; Y = Br_2/$CHCl_3$, 0°C

Sol.

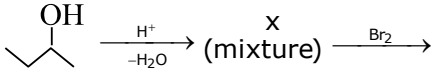
Q.11 

[IIT '2003]

(A)  (B) 

(C) $C_6H_5-\underset{\underset{OH}{|}}{C}=CHCH_3$ (D) $C_6H_5-CH=\underset{\underset{OH}{|}}{C}-CH_3$

Sol.

Q.12 

5 compounds of molecular formula $C_4H_8Br_2$
Number of compounds in X will be:
[IIT '2003]

(A) 2 (B) 3
(C) 4 (D) 5

Sol.

Q.13 2–hexyne can be converted into trans–2–hexene by the action of : **[IIT '2004]**

(A) H_2–Pd-$BaSO_4$ (B) Li in liq. NH_3
(C) H_2–PtO_2 (D) $NaBH_4$

Sol.

Q.14 2-phenyl propene on acidic hydration, gives **[IIT '2004]**

(A) 2-phenyl-2-propanol
(B) 2-phenyl-1-propanol
(C) 3-phenyl-1-propanol
(D) 1-phenyl-2-propanol

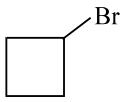
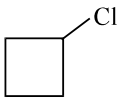
Sol.

Q.15 How many chiral compounds are possible on mono chlorination of 2-methyl butane ? **[IIT '2004]**

(A) 2 (B) 4
(C) 6 (D) 8

Sol.

Q.16 1–bromo–3–chlorocyclobutane when treated with two equivalents of Na, in the presence of ether which of the following will be formed? **[IIT '2005]**

(A)  (B) 

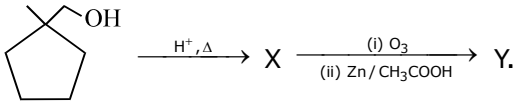
(C)  (D) 

Sol.

Q.17 Cyclohexene is best prepared from cyclohexanol by which of the following **[IIT '2005]**

(A) conc. H_3PO_4 (B) conc. HCl/$ZnCl_2$
(C) conc. HCl (D) Conc. HBr

Sol.

Q.18 

Identify X and Y. **[IIT 2005]**

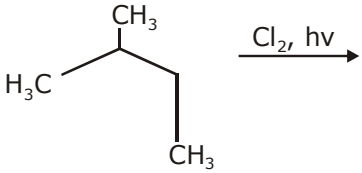
Sol.

Q.19 CH_3–CH=CH_2 + NOCl $\rightarrow$ P Identify the adduct. **[IIT 2006]**

(A) $CH_3-\underset{\underset{Cl}{|}}{CH}-\underset{\underset{NO}{|}}{CH_2}$ (B) $CH_3-\underset{\underset{NO}{|}}{CH}-\underset{\underset{Cl}{|}}{CH_2}$

(C) $CH_3-CH_2-\underset{\displaystyle Cl}{\overset{\displaystyle NO}{\underset{|}{\overset{|}{CH}}}}$ (D) $CH_2-\underset{\displaystyle NO}{\underset{|}{CH_2}}-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH_2}}$

Sol.

Q.20  N(isothermeric products) $C_5H_{11}Cl \xrightarrow{\text{fractional distillation}}$ M(isomeric products). What are N and M ? **[IIT '2006]**

(A) 6, 6 (B) 6, 4
(C) 4, 4 (D) 3, 3

Sol.

Q.21 The number of structural isomers for C_6H_{14} is **[IIT 2007]**

(A) 3 (B) 4
(C) 5 (D) 6

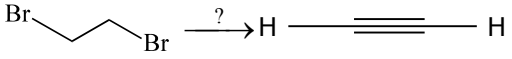
Sol.

Q.22 The number of stereoisomers obtained by bromination of trans-2-butene is **[IIT 2007]**

(A) 1 (B) 2
(C) 3 (D) 4

Sol.

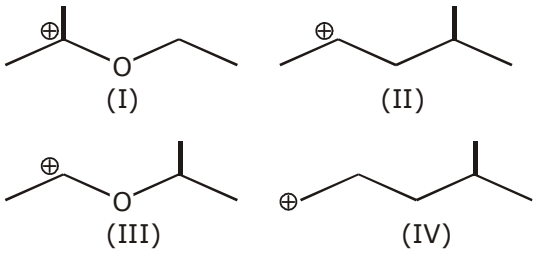
Q.23 The reagent(s) for the following conversion, **[IIT 2007]**



is / are
(A) alcoholic KOH
(B) alcoholic KOH followed by $NaNH_2$
(C) aqueous KOH followed by $NaNH_2$
(D) Zn / CH_3OH

Sol.

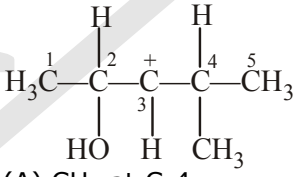
Q.24 The correct stability order for the following species is **[IIT '2008]**



(A) II > IV > I > III (B) I > II > III > IV
(C) II > I > IV > III (D) I > III > II > IV

Sol.

Q.25 In the following carbocation, H/ CH_3 that is most likely to migrate to the positively charged carbon is **[IIT 2009]**



(A) CH_3 at C-4
(B) H at C-4
(C) CH_3 at C-2
(D) H at C-2

Sol.

Q.26 Intermediate produced when propene react with HCl in presence of peroxide **[IIT 2009]**

(A) $CH_3-CH_2-\overset{\oplus}{C}H_2$
(B) $CH_3-\overset{\oplus}{C}H-CH_3$
(C) $CH_3-CH_2\overset{\bullet}{C}H_2$
(D) $CH_3-\overset{\bullet}{C}H-CH_3$

Sol.

Q.27 The total number of cyclic isomers possible for a hydrocarbon with the molecular formula C_4H_6 is **[IIT 2010]**

Sol.

Q.28 In Allene (C_3H_4), the type (s) of hybridisation of the carbon atoms is (are) **[IIT 2012]**

(A) sp and sp^3 (B) sp and sp^2

(C) only sp^2 (D) sp^2 and sp^3

Q.29 Carry out the following transformation in not more than three steps.**[IIT 1999]**

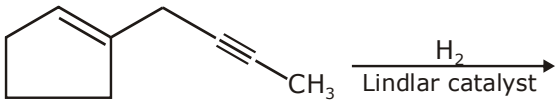
$CH_3-CH_2-C\equiv C-H \rightarrow CH_3-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$

Sol.

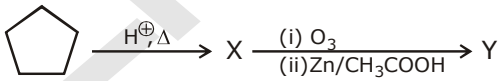
Q.30 $CH_2=CH^-$ is more basic than $HC\equiv C^-$ **[IIT 2000]**

Sol.

Q.31 What would be the major product in each of the following reactions?**[IIT 2000]**



Sol.

Q.32 

Identify X and Y. **[IIT 2005]**

Sol.

Q.33 The total number alkenes possible by dehydrobromination of 3-bromo-3-cyclopentylhexane using alcoholic KOH is . **[IIT 2011]**

Sol.

Answers

Exercise-I

1. B	2. A	3. B	4. C	5. B	6.B	7. A
8.A	9. C	10. C	11. D	12. D	13. C	14. C
15. B	16. D	17. C	18. D	19. A	20. B	21. B
22. C	23. A	24. D	25. A	26. A	27. A	28. A
29. B	30. C	31. C	32. A	33. B	34. C	35. B
36. C D	37. ABCD	38. C D	39. ACD	40. ABD	41. T	42. F

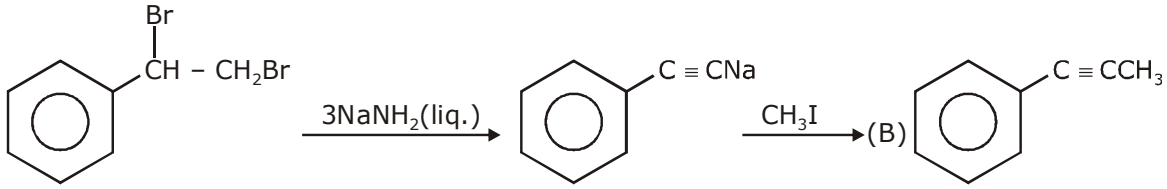
Exercise-II

1. D	2. D	3. A	4. D	5. B	6. B	7. B
8. A	9. D	10. A	11. C	12. C	13. C	14. D
15. D	16. D	17. B	18. D	19. C	20. D	21. C
22. C	23. A	24. D	25. D	26. D	27. B	28. B
29. D	30. A	31. C	32. A	33. C	34. D	35. A
36. B	37. B	38. A	39. C	40. B	41. C	42. B
43. B	44. D	45. A	46. A	47. A	48. A	49. C
50. B	51. C	52. C	53. B	54. B		

Exercise-III

1. D	2. A	3. D	4. A	5. A	6. B	7. C
8. D	9. C	10. A	11. C	12. D	13. C	14. B
15. B	16. A	17. A,C,D	18. A,C	19. A.C	20. A,B	21. A,C

22. 44 + 2 = 46

23. (A) 

24. (a) 2 (b) 2 (c) 2

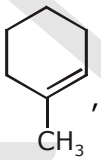
Exercise-IV (PREVIOUS YEARS PROBLEMS)

Level-I (JEE MAIN)

1. B	2. A	3. B	4. B	5. B	6. C	7. C
8. D	9. C	10. A	11. A	12. D	13. A	14. A
15. A	16. A	17. A	18. C	19. C	20. A	21. B
22. C	23. A	24. A				

Level-II (JEE ADVANCED)

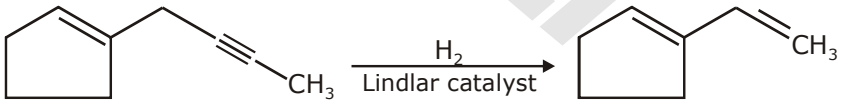
1. A	2. D	3. C	4. C	5. B	6. B	7. B
8. B	9. D	10. B	11. A	12. B	13. B	14.A

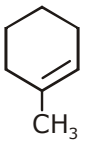
15. B 16. D 17. A 18. (x) =  , (Y) = $CH_3 - \overset{O}{\overset{\|}{C}} - (CH_2)_4 - CH = O$

19. A	20. B	21. C	22. A	23. B	24. D	25. D
26. B	27. 5	28. B	29.	(1) $NaNH_2$, (2) Me – I (3) $HgSO_4$ dil H_2SO_4		

30. higher electronegativity of sp carbon

31. In presence of Lindlar's catalyst (Pd and $CaCO_3$ in quinoline) partial hydrogenation takes place and cis isomer is obtained.



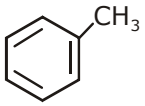
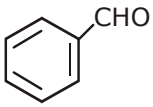
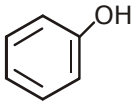
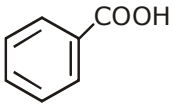
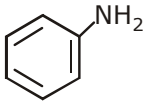
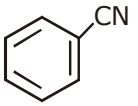
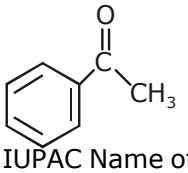
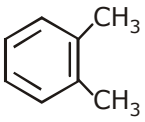
32. (X) 

(Y) $CH_3 - \overset{O}{\overset{\|}{C}} - (CH_2)_4 - CH = O$

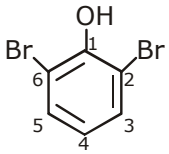
33. 5

AROMATIC COMPOUND

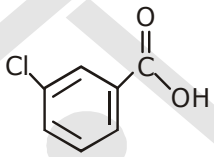
some important aromatic compounds with their common names.

Formula	Name	Formula	Name
	**Toluene (bp 111 °C)**		**Benzaldehyde (bp 178 °C)**
	**Phenol (mp 43 °C)**		**Benzoic acid (mp 122 °C)**
	**Aniline (bp 184 °C)**		**Benzonitrile (bp 191 °C)**
	**Acetophenone (mp 21 °C)**		**Ortho-xylene (bp 144 °C)**

IUPAC Name of Substituted phenol and benzoic acid.

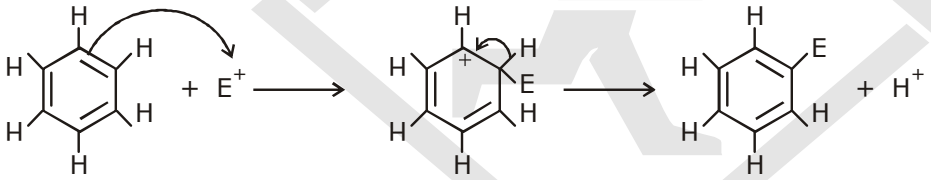


2,6-Dibromophenol



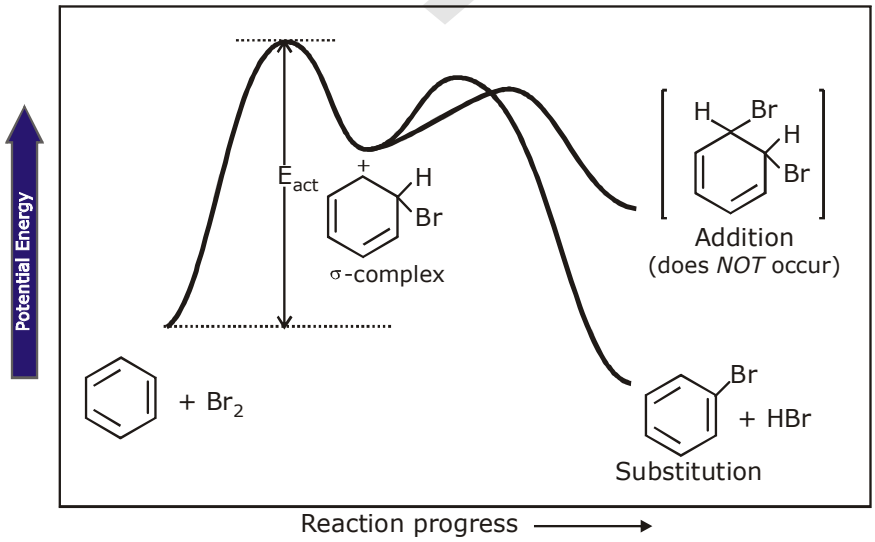
m-chlorobenzoic acid

Electrophilic Aromatic Substitution Reaction

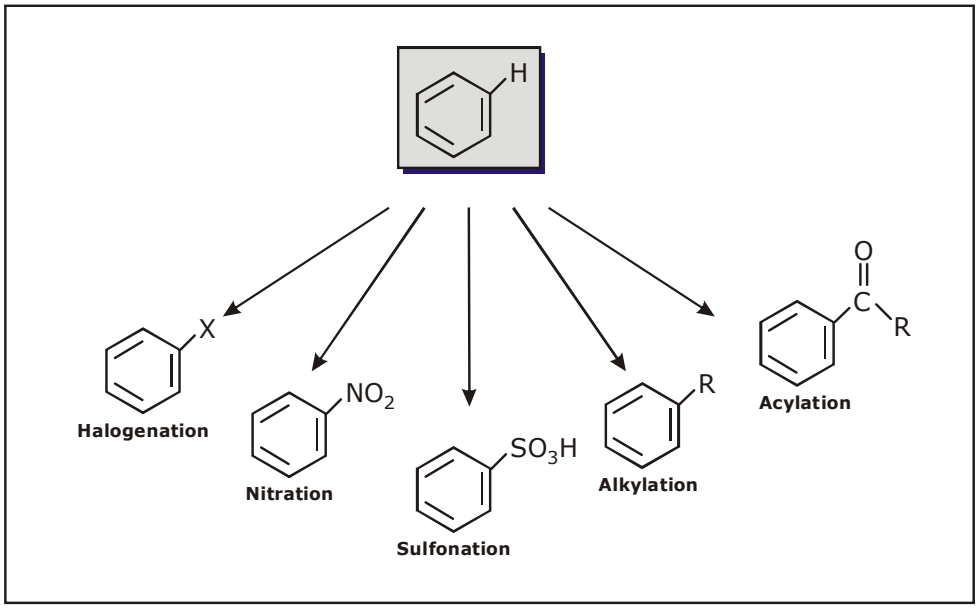


σ-complex

A reaction energy diagram for the electrophilic bromination of benzene. The reaction occurs in two steps and releases energy.



Some Electrophilic Aromatic substitution reactions:



(i) **Ortho- and para-directing activators :** Groups like –OH ad $–NH_2$ present on a ring direct an electrophile, E^+, to ortho or para position and they react faster than benzene.

(ii) **Ortho- and para-directing deactivators :** Helogens present on a ring direct an electrophile, E^+, to ortho or para positions, and they react slower than benzene.

(iii) **Meta-directing deactivators :** Groups containing a carbonyl (C = O) or a –CN group direct an electrophile, E^+, to the meta positions, *but* they react slower than benzene.

No meta-directing activators are known. Figure 5.8 shows how the directing effects of the groups correlate with their reactivities. All meta directing grops are deactivating and most ortho-and para-directing groups are activating. The halogens are unique in being ortho and para directing *and* deactivating.

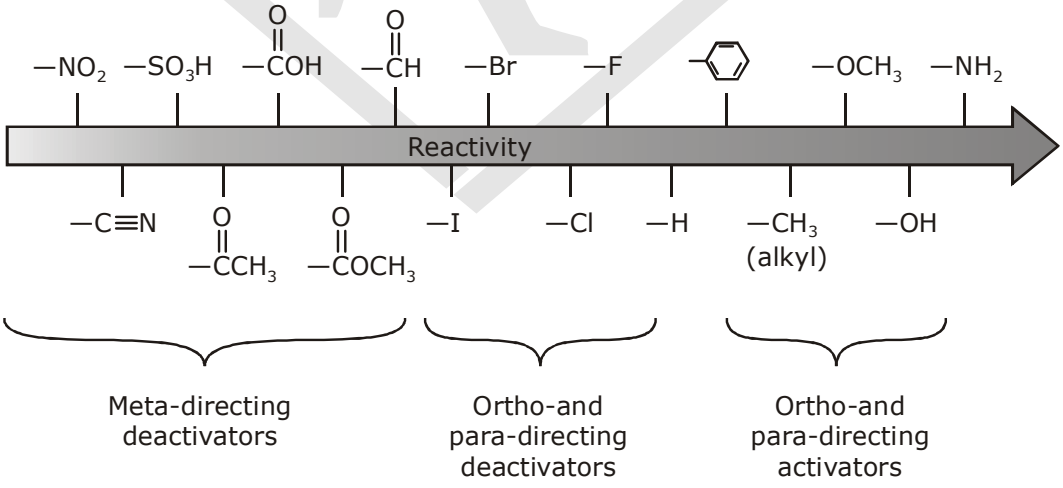
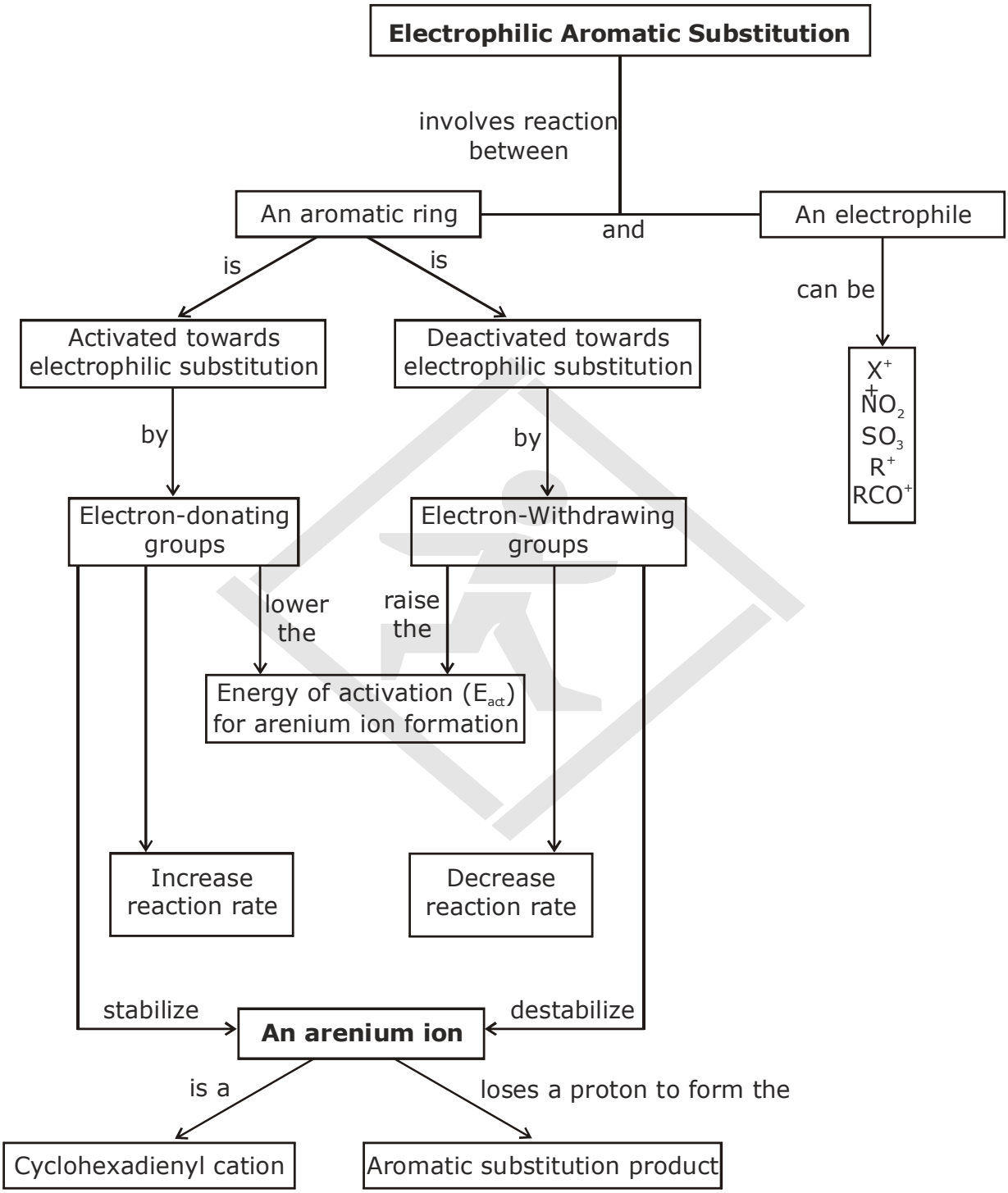


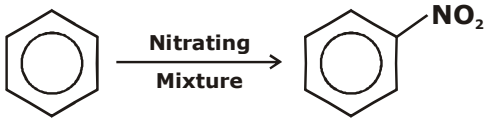
Figure Substituent effects in electrophilic aromatic substitutions. All activating groups are ortho-and para-directing, and all deactivating groups other than halogen are meta-directing. The halogens are ortho and para-directing deactivators.

CONCEPT MAP


Electrophilic Aromatic Substitution
involves reaction between
An aromatic ring
and
An electrophile
is
is
can be
Activated towards electrophilic substitution
Deactivated towards electrophilic substitution
X^+
NO_2^+
SO_3
R^+
RCO^+
by
by
Electron-donating groups
Electron-Withdrawing groups
lower the
raise the
Energy of activation (E_{act}) for arenium ion formation
Increase reaction rate
Decrease reaction rate
stabilize
destabilize
An arenium ion
is a
loses a proton to form the
Cyclohexadienyl cation
Aromatic substitution product

EXERCISE – I OBJECTIVE PROBLEMS (JEE MAIN)

Single Choice Questions :

1. 

Given reaction is an example of

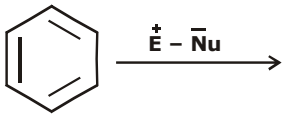
(A) Substitution electrophilic aromatic (SEAr)

(B) Substitution nucleophilic aromatic (SNAr)

(C) Electrophilic addition reaction (EAR)

(D) Bi molecular nucleophilic substution (SN_2)

Sol.

2. 

Name of intermediate produced during given reaction will be

(A) Arenium ion

(B) σ-complex/wheeland intermediate

(C) Nonaromatic cyclohexa dienyl carbocation

(D) All of these

Sol.

3. Which of the following reagent is best when friedel craft Halogenation takes place

(A) HO^- (B) $AlCl_3$ (anhyd.)
(C) $AlCl_3$ (hydrated) (D) All of these

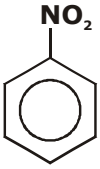
Sol.

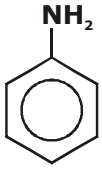
4. WHat is the name of electrophile when benzene goes nitration

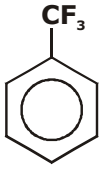
(A) Nitrosonium ion (B) Nitronium ion
(C) Halonium ion (D) Alkyl carbocation

Sol.

5. Which of the following compound gives poor yield in friedel-craft reaction

(A) 

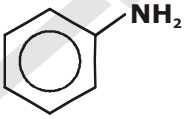
(B) 

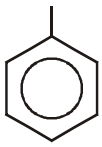
(C) 

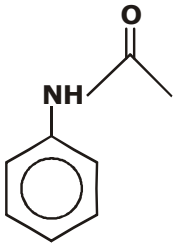
(D) All of these

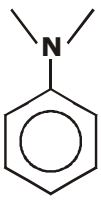
Sol.

6. Most reactive towards nitration reaction (Substitution electrophilic aromatic)

(A) 

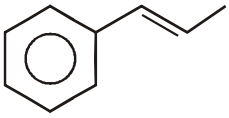
(B) 

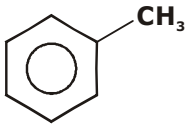
(C) 

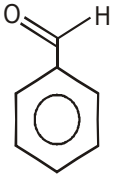
(D) 

Sol.

7. Which of the following compound gives benzoic acid when it reacts with hot $KMnO_4$ followed by acidification.

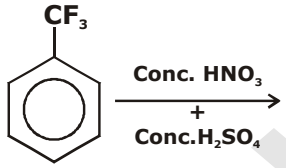
(A) 

(B) 

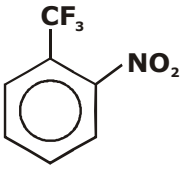
(C) 

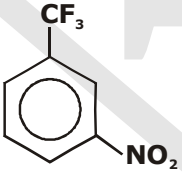
(D) All of these

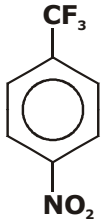
Sol.

8. 

Major product

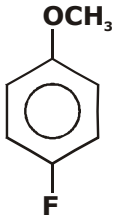
(A) 

(B) 

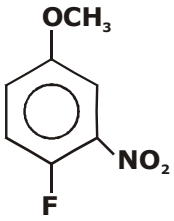
(C) 

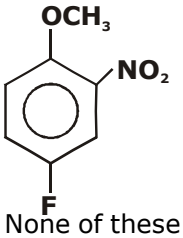
(D) A and C both

Sol.

9. 

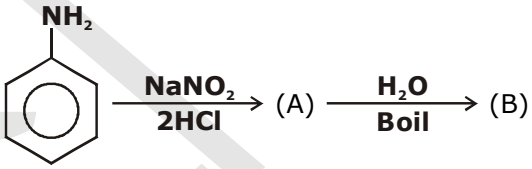
Nitration Major product

(A) 

(B) 

(C) Mixture A and B (D) None of these

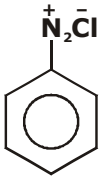
Sol.

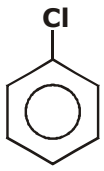
10. 

Product (B) will be :

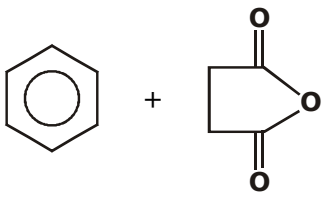
(A) 

(B) 

(C) 

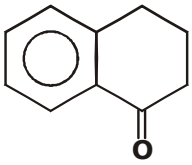
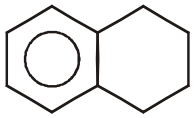
(D) 

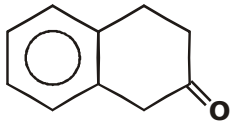
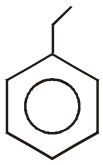
Sol.

11.  $\xrightarrow{AlCl_3}$ (A)

$\xrightarrow[HCl]{Zn(Hg)}$ (B) $\xrightarrow{conc.H_2SO_4}$ (C) (Major product)

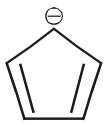
C will be :

(A)  (B) 

(C)  (D) 

Sol.

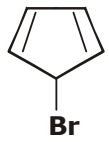
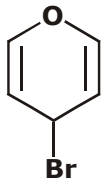
12. How many π electron are there in the following speices :

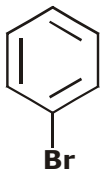
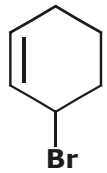


(A) 2 (B) 4
(C) 6 (D) 8

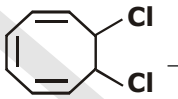
Sol.

13. Ease of ionization to produce carbocation and bromide ion under the treatment of $Ag^{\oplus}$ will be maximum in ?

(A)  (B) 

(C)  (D) 

Sol.

14.  $\xrightarrow{2SbCl_5}$ P ; P will be

(A)  (B) 

(C)  (D) Mixture of A & B

Sol.

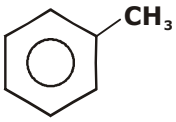
15. Which order is correct for the decreasing reactivity to ring monobromination of the following compounds :

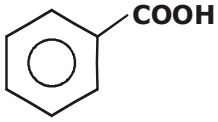
(I) $C_6H_5CH_3$ (II) C_6H_5COOH
(III) C_6H_6 (IV) $C_6H_5NO_2$

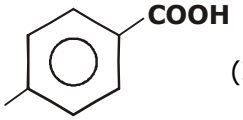
(A) I > II > III > IV (B) I > III > II > IV
(C) II > III > IV > I (D) III > I > II > IV

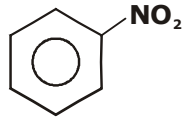
Sol.

16. Which of the following order is correct for the decreasing reactivity to ring monobromination of the following compounds :

(I) 

(II) 

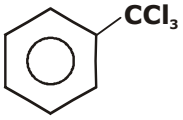
(III) 

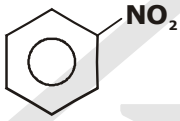
(IV) 

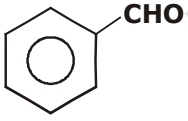
(A) I > II > III > IV (B) II > III > IV > I
(C) I > III > II > IV (D) III > I > II > IV

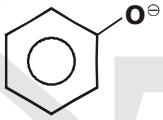
Sol.

17. Electrophile $\overset{\oplus}{N}O_2$ attacks the following :

(I) 

(II) 

(III) 

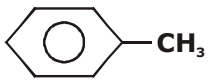
(IV) 

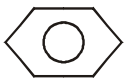
In which cases $\overset{\oplus}{N}O_2$ will attack at meta position

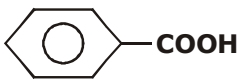
(A) II and IV (B) I, II and III
(C) II and IV (D) I only

Sol.

18. Increasing order of the following for electrophile substitution reaction as -

(I) 

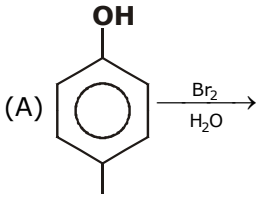
(II) 

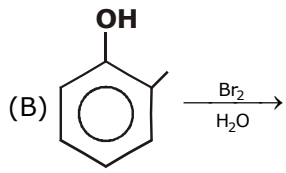
(III) 

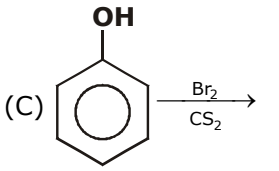
(A) I > II > III (B) III > II > I
(C) II > III > I (D) I > III > II

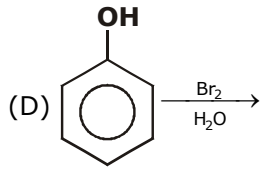
Sol.

19. Which of the following will form tri-bromo derivative of phenol ?

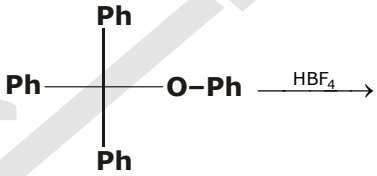
(A) 

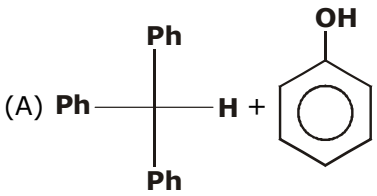
(B) 

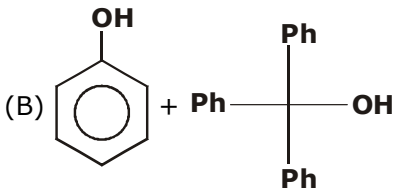
(C) 

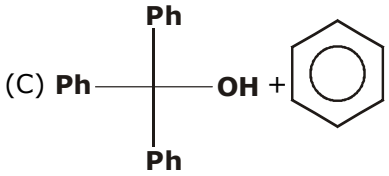
(D) 

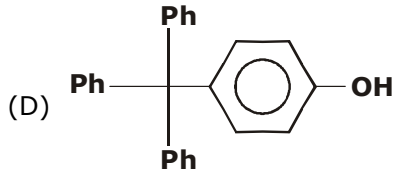
Sol.

20.  Product of this reaction is :

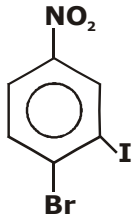
(A) 

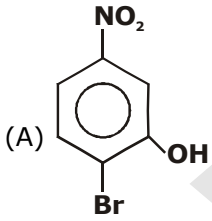
(B) 

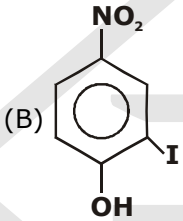
(C) 

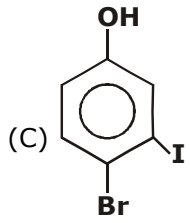
(D) 

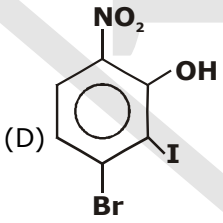
Sol.

21.  $\xrightarrow[(2)H_3O^{\oplus}]{(1)NaOH\,\Delta}$ (A), Product (A) is

(A) 

(B) 

(C) 

(D) 

Sol.

22. For preparing monoalkyl benzene, acylation process is preferred than direct alkylation because

(A) In alkylation, a poisonous gas is evolved

(B) In alkylation, large amount of heat is evolved

(C) In alkylation, pollyalkylated product is formed

(D) Alkylation is very costly

Sol.

23. Benzene reacts with n-propyl chloride in the presence of anhydrous $AlCl_3$ to give predominantly :

(A) n-Propylbenzene
(B) Isopropylbenzene
(C) 3-Propyl-1-Chlorobenzene
(D) No reaction

Sol.

24. In the sulphonation, acetylation and formylation of benzene the group of effective electrophiles would be :

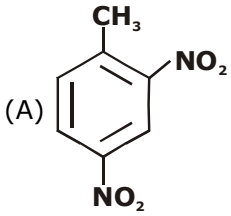
(A) SO_3^+, $CH_3C \equiv O^+$, $H\overset{+}{C}O$

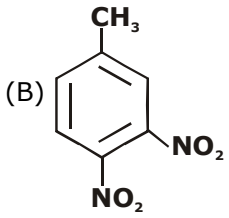
(B) SO_3, $CH_3 - C \equiv O^+$, $H\overset{+}{C}O$

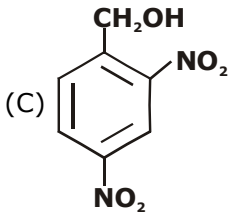
(C) SO_3, CH_3CHO, $CO + HCl$
(D) HSO_3, CH_3CO, HCO

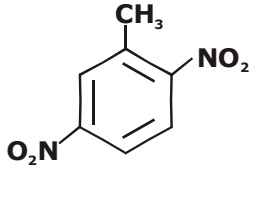
Sol.

25. p-Nitrotoluene on further nitration gives :

(A) 

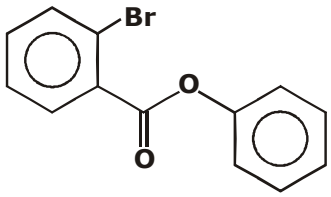
(B) 

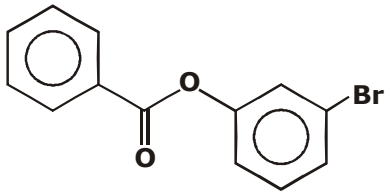
(C) 

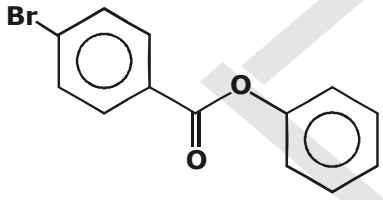
(D) 

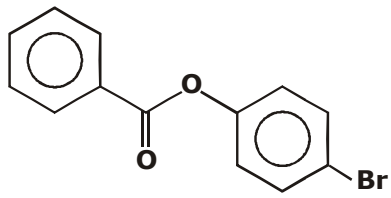
Sol.

26. The major product formed on monobromination of phenylbenzoate is :

(A) 

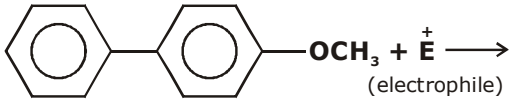
(B) 

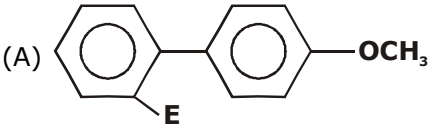
(C) 

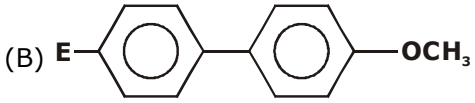
(D) 

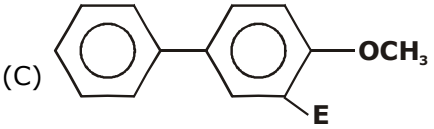
Sol.

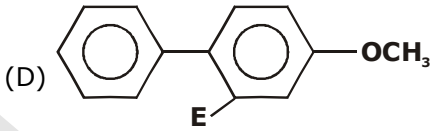
27. The major product formed in the reaction is :



(A) 

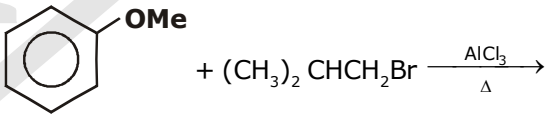
(B) 

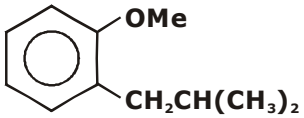
(C) 

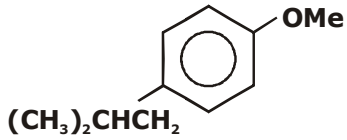
(D) 

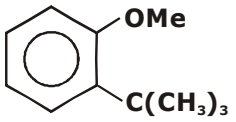
Sol.

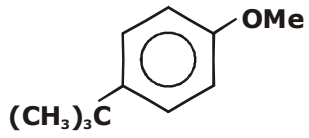
28. The major product formed in the reaction is :



(A) 

(B) 

(C) 

(D) 

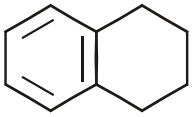
Sol.

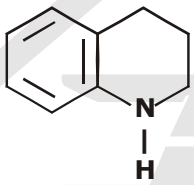
29. In the sulhponation of benzene, the active electrophilic species is :

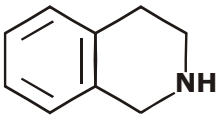
(A) SO_2 (B) SO_3
(C) SO_4^{2-} (D) HSO_4^-

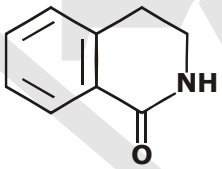
Sol.

30. Which one of the following compounds undergoes bromination of its aromatic ring at the fastest rate ?

(A) 

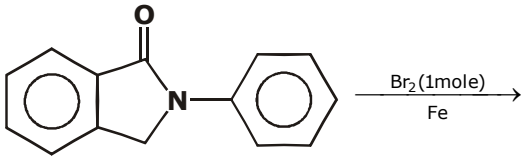
(B) 

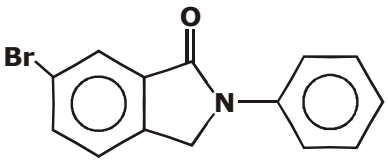
(C) 

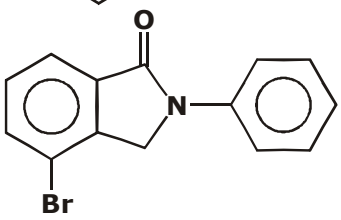
(D) 

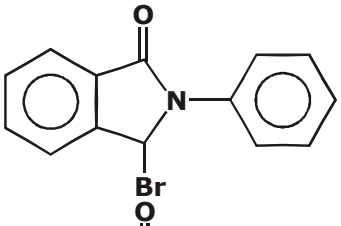
Sol.

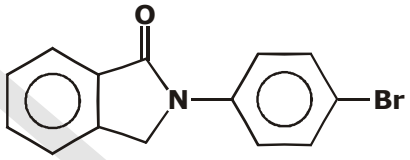
31. In the reaction the major product formed is :



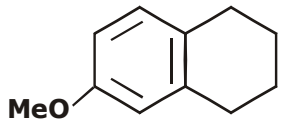
(A) 

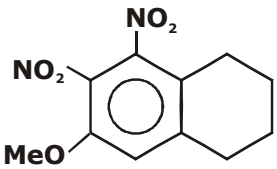
(B) 

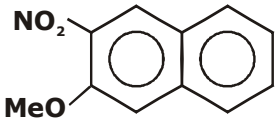
(C) 

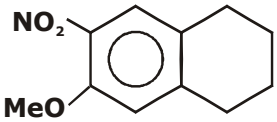
(D) 

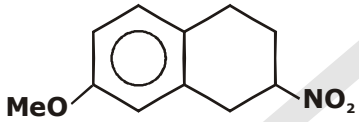
Sol.

32.  $\xrightarrow{HNO_3/H_2SO_4}$ (A) Major product :

(A) 

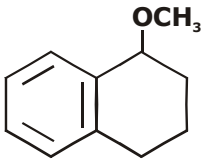
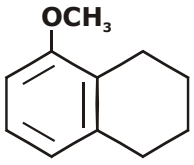
(B) 

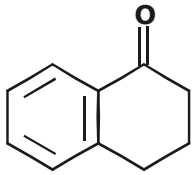
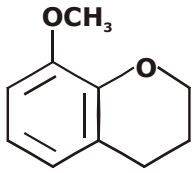
(C) 

(D) 

Sol.

33. Increasing order of rate of reaction with Br_2/ $AlBr_3$ is :

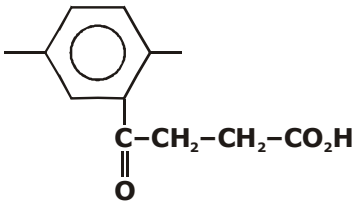
(I)  (II) 

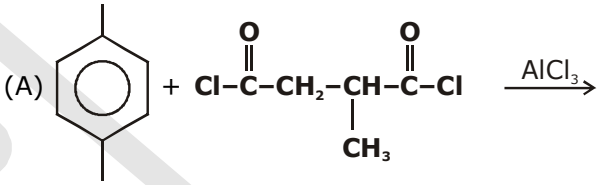
(III)  (IV) 

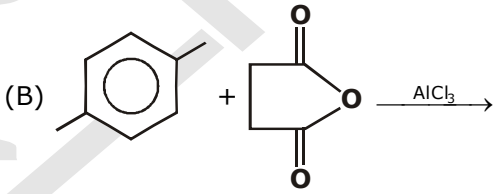
(A) III < I < II < IV (B) III < II < I < IV
(C) II < IV < III < I (D) IV < II < III < I

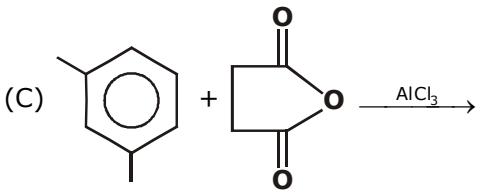
Sol.

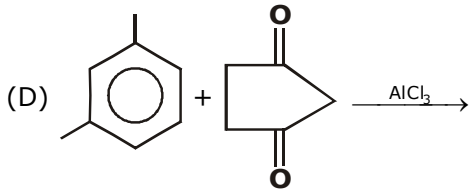
34. What combiantion of acid chloride or anhydride and arene would you choose to prepare given compound ?



(A) 

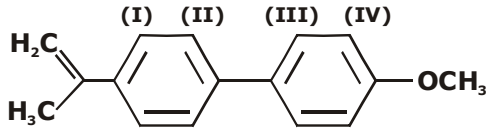
(B) 

(C) 

(D) 

Sol.

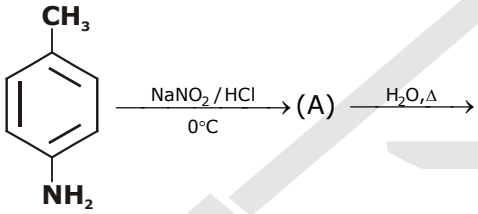
35. Which position will be attacked most rapidly by the nitronium ion (NO_2^+) when the compound undergoes nitration with HNO_3/H_2SO_4 :

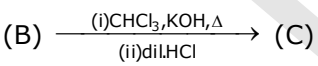


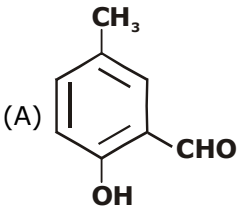
(A) I (B) II
(C) III (D) IV

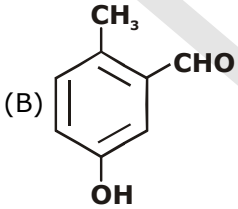
Sol.

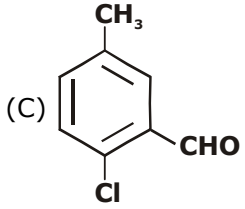
36. Identify (C) in the reaction(s)







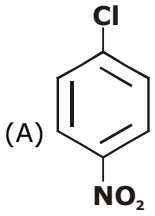


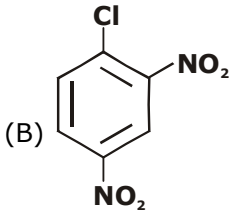


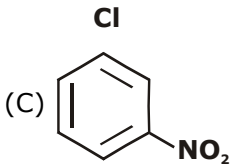
(D) None of these

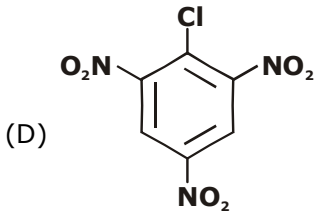
Sol.

37. Which of the following is most reactive toward SNAr :

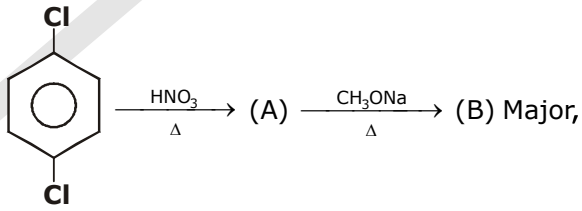




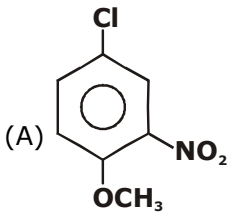


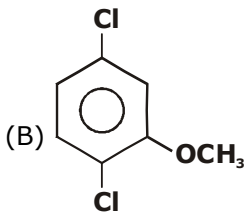


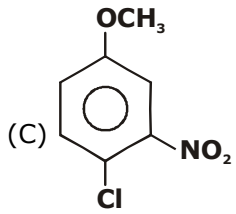
Sol.

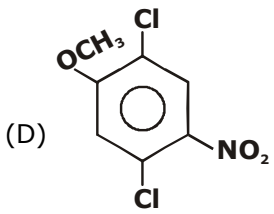
38. 

Product (B) is



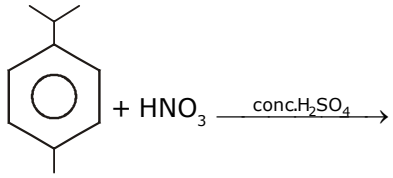


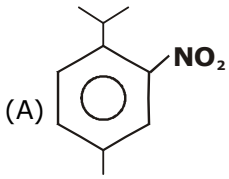


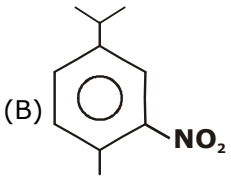


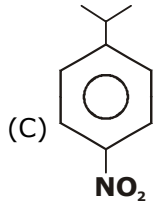
Sol.

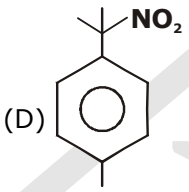
39. The major product formed in the reaction is :



(A) 

(B) 

(C) 

(D) 

Sol.

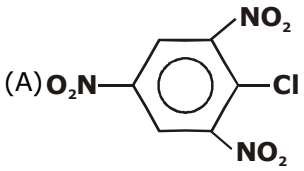
40. $C_6H_5CH_3 \xrightarrow{CrO_2Cl_2} A \xrightarrow{H_2O} B$

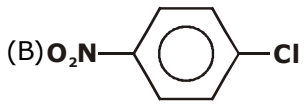
The functional group present in B and name of the reaction would be

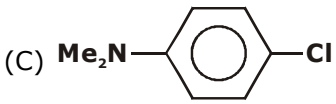
(A) –CHO, Gattermann aldehyde synthesis
(B) –CHO, Etard reaction
(C) $-COCH_3$, Fridel Crafts reaction
(D) –CHO, Oxo reaction

Sol.

41. Which chloroderivative of benzene among the following would undergo-hydrolysis most readily with aq. NaOH to furnish the corresponding hydroxy derivative.

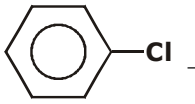
(A) 

(B) 

(C) 

(D) 

Sol.

42. Chloral +  $\xrightarrow{conc.H_2SO_4}$ product. The produt is :

(A) Lindane (B) DDT
(C) Caprolactum (D) Nylon-6

Sol.

43. $C_6H_6 + A \xrightarrow{AlCl_3} C_6H_5CONH_2$

A in the above reaction is :

(A) NH_2CONH_2 (B) $ClCONH_2$
(C) CH_3CONH_2 (D) $CH_2(Cl)CONH_2$

Sol.

44. $C_6H_6 \xrightarrow[AlCl_3]{CH_3COCl} A \xrightarrow[HCl]{Zn-Hg} B$

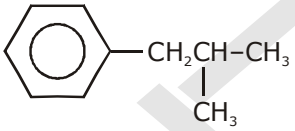
The end product in the above sequence is :

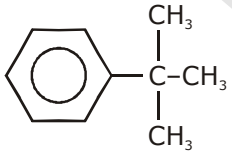
(A) Toluene (B) Ethyl benzene
(C) Both the above (D) None

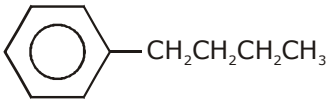
Sol.

45.  + $CH_3-CH_2-CH_2-CH_2-Cl \xrightarrow{AlCl_3}$

hydrocarbon (X) major product X is

(A) 

(B) 

(C) 

(D) None of correct

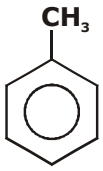
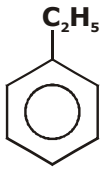
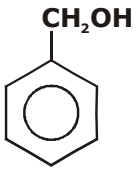
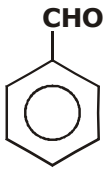
Sol.

46. Reaction of SO_3 is easier in :

(A) Benzene (B) Toluene
(C) Nitrobenzene (D) chlorobenzene

Sol.

47. The mixture of the following four aromatic compounds on oxidation by strong oxidising agent gives :




and


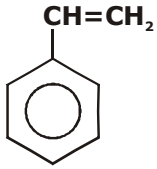
(A) Mixture of $C_6H_5CH_2OH + C_6H_5COOH$
(B) Mixture of $C_6H_5CHO + C_6H_5COOH$
(C) C_6H_5COOH
(D) None of the above

Sol.

48. Methyl group attached to benzene can be oxidised to carboxyl group by reacting with :

(A) Fe_2O_3 (B) $AgNO_3$
(C) $KMnO_4$ (D) CrO_3

Sol.

49. A  B

Compound A and B respectively are :

(A) o-Bromostyrene, benzoic acid
(B) p-Bromostyrene, benzaldehyde
(C) m-Bromostyrene, benzaldehyde
(D) Styrene dibromide, benzoic acid

Sol.

50. The number of benzylic hydrogen atoms in ethylbenzene is :

(A) 3 (B) 5
(C) 2 (D) 7

Sol.

51. The highest yield of m-product is possible by the electrophilic substitution of the following :

(A) $C_6H_5CH_3$
(B) $C_6H_5CH_2COOC_2H_5$
(C) $C_6H_5CH(COOC_2H_5)_2$
(D) $C_6H_5C(COOC_2H_5)_3$

Sol.

52.  + H_2 $\xrightarrow[\text{high pressure}]{\text{Ni,High temp.}}$ (A). Which of the following can be isolated as the product of this reaction.

(A) 
(B) 
(C) 
(D) 

Sol.

53. Which of the following is/are produced when a mixture of benzene vapour and oxygen is passed over V_2O_5 catalyst at 775 K ?

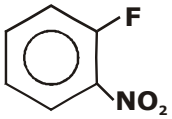
(A) Oxalic acid (B) Glyoxal
(C) Fumaric acid (D) Maleic anhydride

Sol.

54. Which of the following is the least reactive in the case of bromination ?

(A) Phenol (B) Aniline
(C) Nitrobenzene (D) Anisole

Sol.

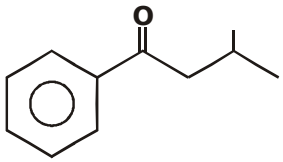
55. 

Above compound undergoes

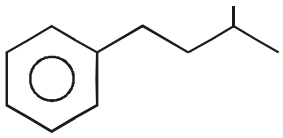
(A) SN_1
(B) SN_2
(C) Elimination
(D) Nucleophilic aromatic substitution

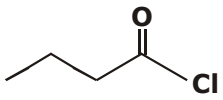
Sol.

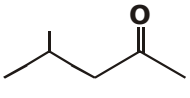
56. Benzene on reaction with 'A' forms

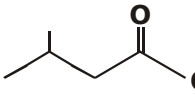


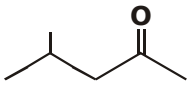
which on reaction with

'B' forms  'A' and 'B' are:

(A) Zn (Hg) + conc. HCl, 

(B)  , $LiAlH_4$

(C)  , $NaBH_4$

(D)  , Zn(Hg) + conc.HCl

+ $AlCl_3$

Sol.

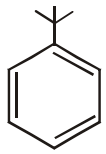
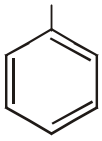
57. In a reaction of C_6H_5Y, the major product (>60%) is m-isomer, so the group Y is :

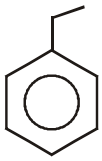
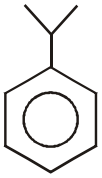
(A) –COOH (B) –Cl

(C) –OH (D) $-NH_2$

Sol.

58. Which of the following will undergo sulphonation at fastest rate ?

(A)  (B) 

(C)  (D) 

Sol.

59. Which of the following is most reactive towards sulphonation ?

(A) m-Xylene (B) o-Xylene

(C) Toluene (D) p-Xylene

Sol.

60. When sulphonilic acid ($p\text{-}H_2NC_6H_4SO_3H$) is treated with excess of bromine water the product is:

(A) tribromo product

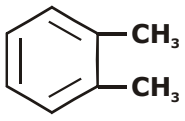
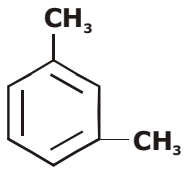
(B) dibromo product

(C) monobromo product

(D) tetrabromo product

Sol.

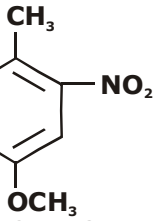
61. Ring nitration of dimethyl benzene results in the formation of only one nitro dimethyl benzene. The dimethyl benzene is :

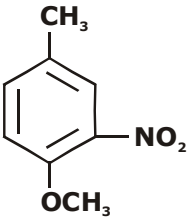
(A)  (B) 

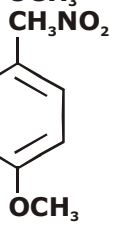
(C)  (D) None of these

Sol.

62. if p-methoxy toluene is nitrated, the major product is :

(A) 

(B) 

(C) 

(D) No reaction

Sol.

63. For the electrophilic substitution reaction involving nitration, which of the following sequence regarding the rate of reaction is true ?

(A) $K_{C_6H_6} > K_{C_6D_6} > K_{C_6T_6}$

(B) $K_{C_6H_6} < K_{C_6D_6} < K_{C_6T_6}$

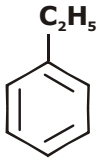
(C) $K_{C_6H_6} = K_{C_6D_6} = K_{C_6T_6}$

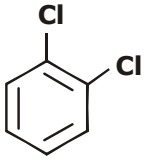
(D) $K_{C_6H_6} > K_{C_6D_6} < K_{C_6T_6}$

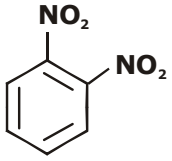
Sol.

64. Identify the correct order of reactivity in electrophilic substitution reactions of the following compunds:

(I) 

(II) 

(III) 

(IV) 

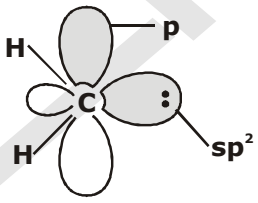
(A) I > II > III > IV (B) IV > III > II > I

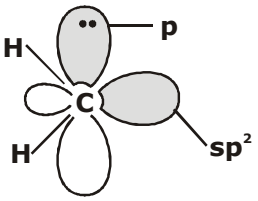
(C) II > I > III > IV (D) II > III > I > IV

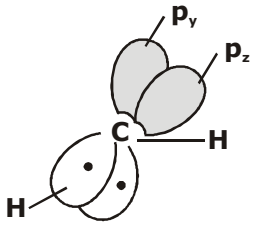
Sol.

CARBENE

65. The orbital picture of a singlet carbene ($:CH_2$) can be drawn as

(A) 

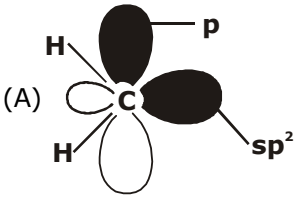
(B) 

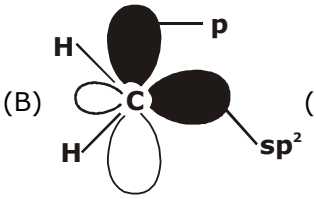
(C) 

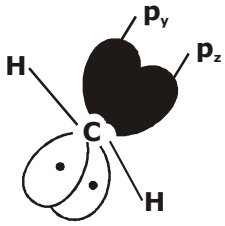
(D) none of these

Sol.

66. The orbital picture of a triplet carbene can be drawn as





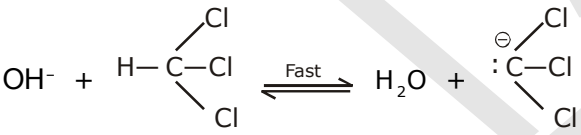


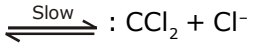
(D) none of these

Sol.

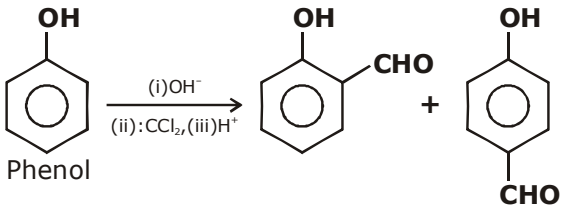
Question No. 67 to 69 (3 questions)

It is believed that chloroform and hydroxide ion react to produce an electron deficient intermediate dichlorocarbene : CCl_2 (DCC)

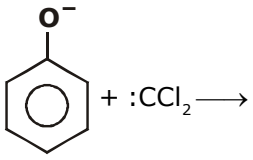


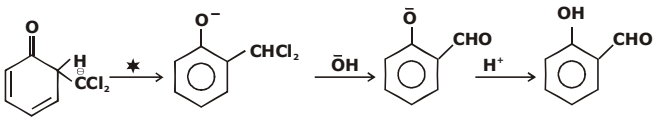


Treatment of phenol with DCC in basic medium introduces an aldehyde group, onto the aromatic ring. This reaction is known as Reimer Tiemann reaction.



The Reimer-Tiemann reaction involves electrophilic substitution on highly reactive phenoxide ring The electrophilic reagent is dichloro carbene :CCl_2.

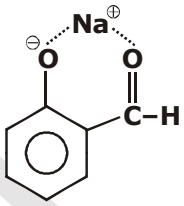




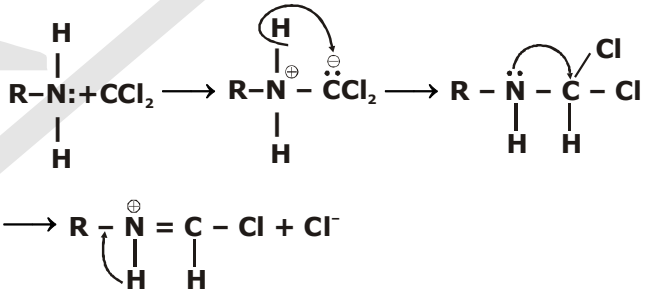
o-product is major product because :

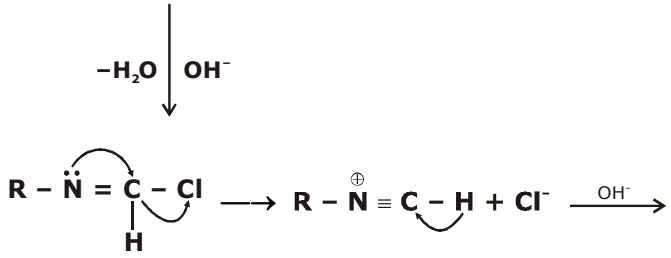
(i) There are two o-positions available as compared to one para.

(ii) o-product is more stable due to the formation ofsix membered chelate formation.



If 1° amines (aliphatic and aromatic) react with DCC in basic medium it yield isocyanide or carbylamine. The reaction is known as carbylamine reaction.





$R - \overset{\oplus}{N} \equiv \overset{\ominus}{C} + H_2O$

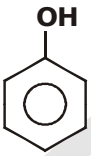
The product is known as isocyanide & it is a foul smelling substance.

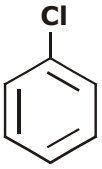
67. Step marked by * is :

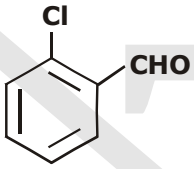
(A) Aromatization reaction
(B) intramolecular acid base reaction

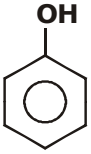
(C) both of the above
(D) none of the above

Sol.

68. If  is used instead of  during Reimer Tiemann reaction the product formed is :

(A) 

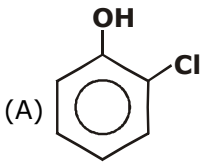
(B) 

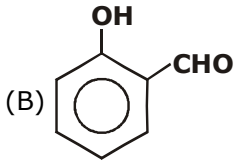
(C) 

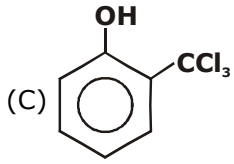
(D) 

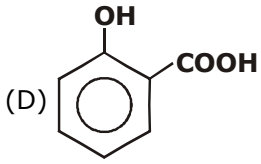
Sol.

69. If CCl_4 is used in place of $CHCl_3$ during Reimer Tiemann reaction, the product formed is:

(A) 

(B) 

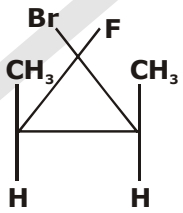
(C) 

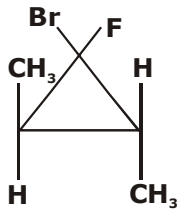
(D) 

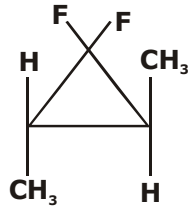
Sol.

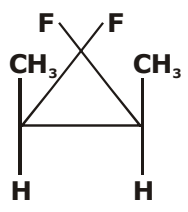
70. $CHF_2Br \xrightarrow{OH^-}$ (A) [Intermediate] $\xrightarrow{\text{Trans–2–butene}}$ (B)

in this reaction B is :

(A) 

(B) 

(C) 

(D) 

Sol.

71. $Ph - \overset{\overset{O}{\|}}{\underset{14}{C}} - CHN_2 \xrightarrow[H_2O]{Ag_2O}$ (A); product (A) is:

(A) $Ph-{}^{14}CH_2-CO_2H$
(B) $Ph-CH_2-{}^{14}CO_2H$
(C) $Ph-{}^{14}CO_2H$
(D) $Ph-CO_2H$

Sol.

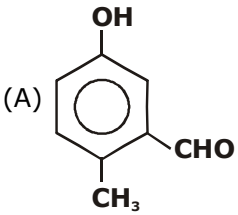
72. Which of the following wil not give carbylamine reaction

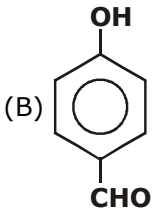
(A) t-butly amine
(B) aniline
(C) sec. butylamine
(D) N-methyl methanamine

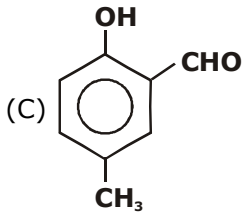
Sol.

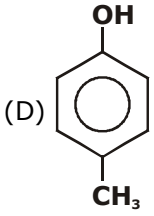
73. 

$\xrightarrow[(ii)\ H^{\oplus}]{(i)\ CHCl_3/KOH}$ (A) Product (A) will be

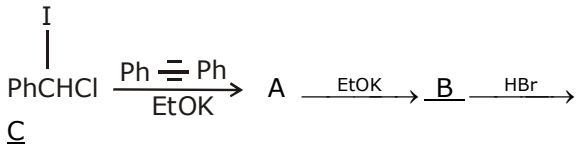
(A) 

(B) 

(C) 

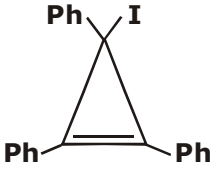
(D) 

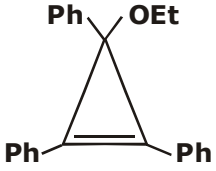
Sol.

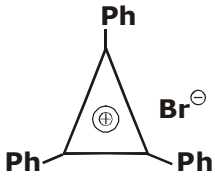
74. 

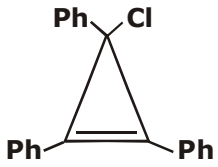
C

correct presentation of C is :

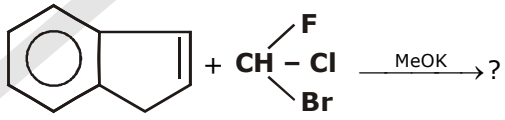
(A) 

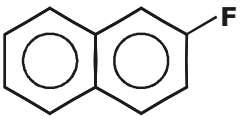
(B) 

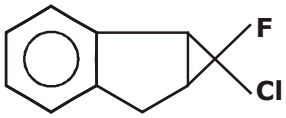
(C) 

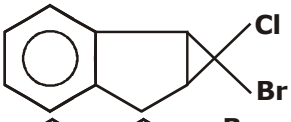
(D) 

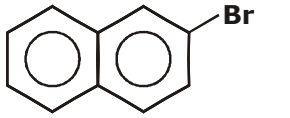
Sol.

75. 

(A) 

(B) 

(C) 

(D) 

Sol.

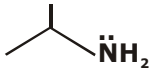
76. Intermediate produced during reimer tiemann's formlylation will be

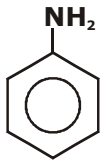
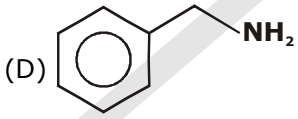
(A) $:CCl_2$ (B) $:CH_2$

(C) $\overset{\ominus}{\underset{\cdot\cdot}{C}}Cl_3$ (D) $CHCl_3$

Sol.

77. Which of the following compound doesn't gives Hoffmann's carbyl amine test ?

(A)  (B) 

(C)  (D) 

Sol.

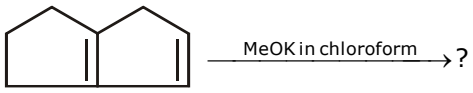
78. $CH_3 - NH_2 + CHCl_3 + KOH \longrightarrow$ major product will be :

(A) $CH_3 - C \equiv N$ (B) $CH_3 - NH - CH_3$

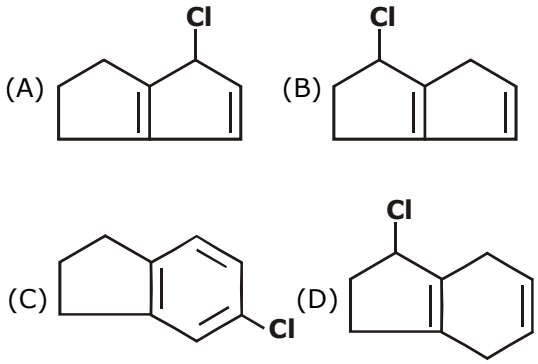
(C) $CH_3 - N^+ \equiv C^-$ (D) NH_3

Sol.

79. What is the product of the following reaction ?



Sol.



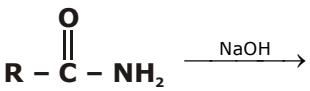
NITRENE

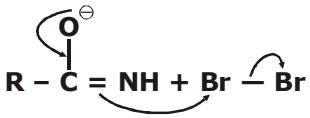
Comprehension (Q.80 to Q.82) (3 Questions)

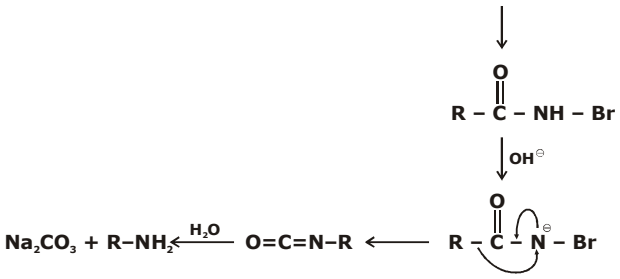
Hoffmann Rearrangment:

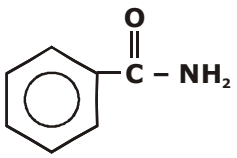
It involves conversion of a carboxylic acid amide into an amine with a loss of a carbon atom on treatment with aqueous sodium hypobromite. THus Hoffmann result in shortening of a carbon chain.

Mechanism of the reaction is







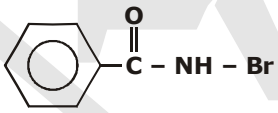
80.  $\xrightarrow[KOH]{Br_2}$ (A) (Major)

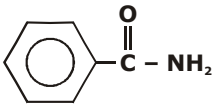
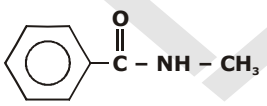
Product (A)

(A) $Ph–NH_2$ (B) $Ph–CH_2–NH_2$
(C) $Ph–NH–CH_3$ (D) $Ph – N(CH_3)_2$

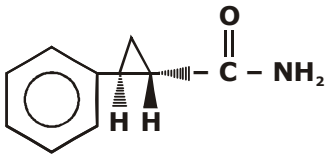
Sol.

81. Which of the following will not given Hoffmann bromamide rection ?

(A)  (B) 

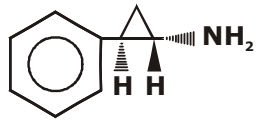
(C)  (D) 

Sol.

82.  $\xrightarrow[\Delta]{Br_2+KOH}$ A (Major)

Product (A) is :

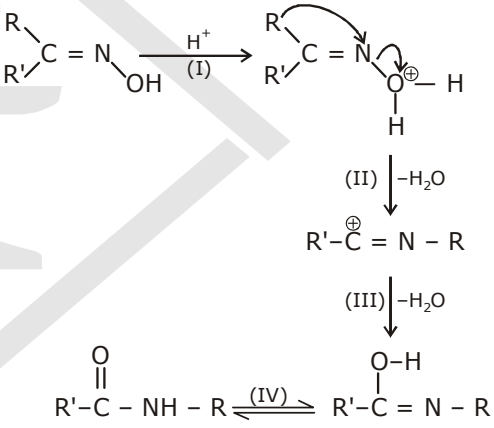
(A)  (B) 

(C)  (D) 

Sol.

Beckmann Rearrangment:

The given is mechanism of Beckmann rearrangment.



83. Reagent cannot be used in Beckmann rearrangement is

(A) H_2SO_4 (B) BF_3
(C) SO_3 (D) OH^-

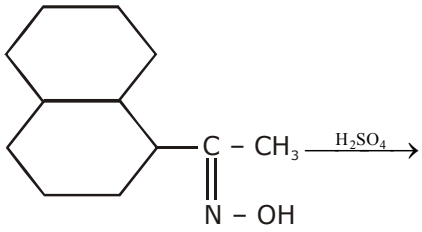
Sol.

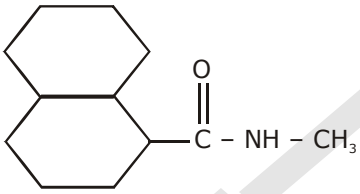
84. Rate determining step in the Beckmann rearrangement is

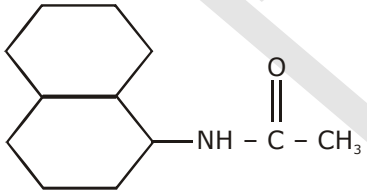
(A) I (B) II
(C) III (D) IV

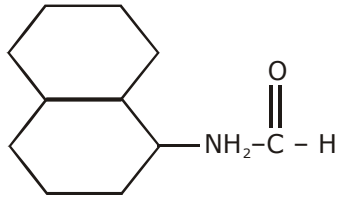
Sol.

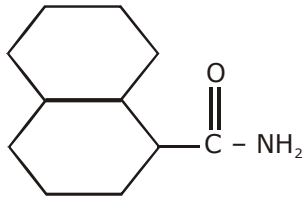
85.



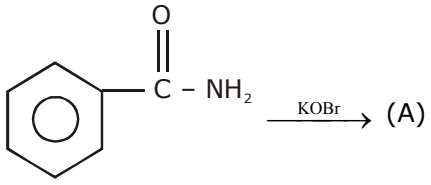
(A) 

(B) 

(C) 

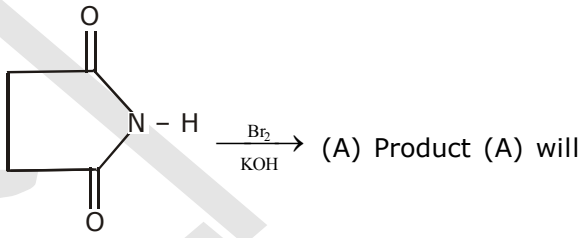
(D) 

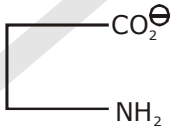
Sol.

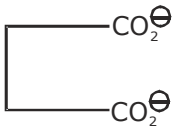
86. 

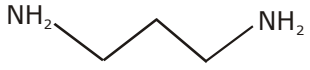
(A) $Ph - CH_2 - NH_2$ (B) $Ph - NH_2$
(C) $Ph - CO_2H$ (D) $Ph - NH - CH_3$

Sol.

87. 

(A) 

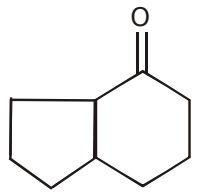
(B) 

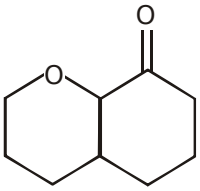
(C) 

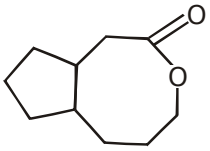
(D) 

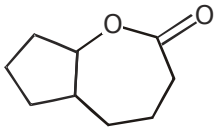
Sol.

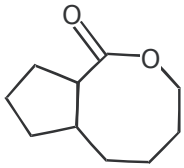
88. Give the major organic product of the following reaction :



(A) 

(B) 

(C) 

(D) 

Sol.

89. 

(X) $\xrightarrow{CF_3CO_3H}$ Major Product (Y) is

(A) $CH_3 - \overset{O}{\overset{\|}{C}} - O - CH_3$

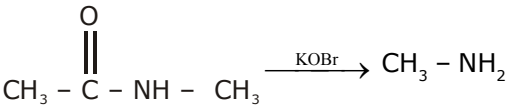
(B) $CH_3 - \overset{O}{\overset{\|}{C}} - O - CH_2 - CH_3$

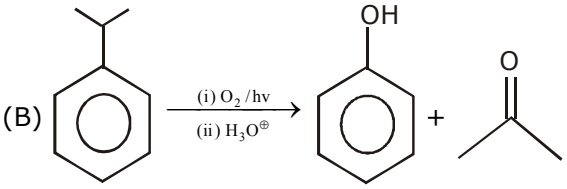
(C) $CH_3 - CH_2 - \overset{O}{\overset{\|}{C}} - O - CH_3$

(D) $CH_3 - CH_2 - CH_2 - O - CH_3$

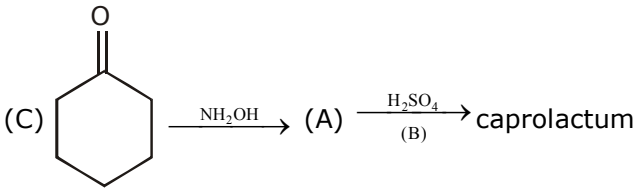
Sol.

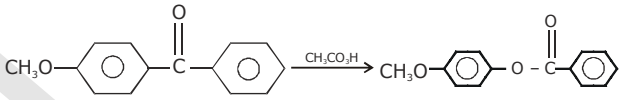
90. Which of the following reaction represent incorrect major product.

(A) 

(B) 

Cumene

(C) 

(D 

Sol.

Exercise - II (One or more than one option correct)

1. An aromatic compound of molecular formula $C_6H_4Br_2$ was nitrated which gives three isomers of formula $C_6H_3Br_2NO_2$ were obtained. The original compound is :

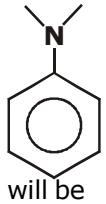
(A) o-dibromobenzene

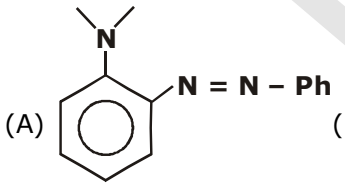
(B) m-dibromobenzene

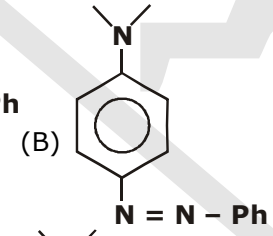
(C) p-dibromobenzene

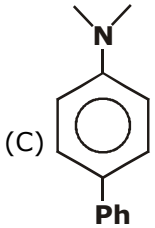
(D) both A and C

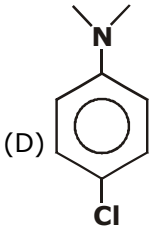
Sol.

2.  $+ Ph - N_2^+Cl^- \longrightarrow$ (A) major product A will be



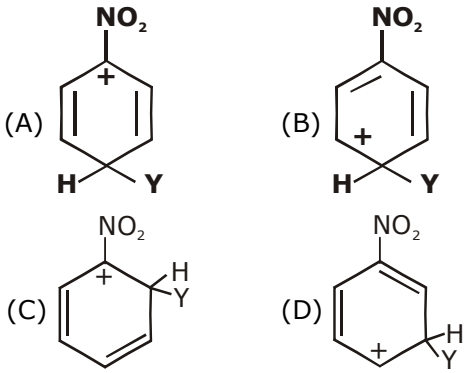






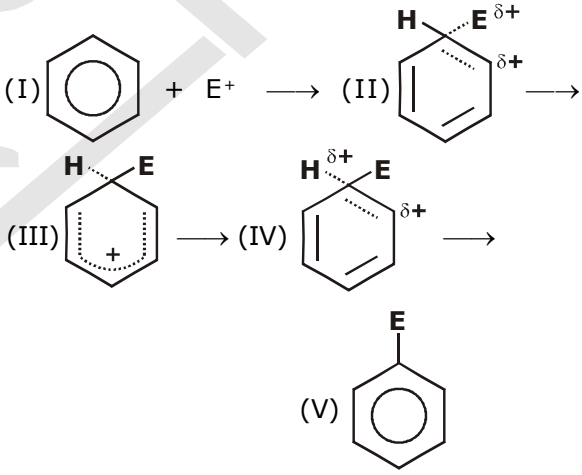
Sol.

3. Which of the following carbocations is expected to be most stable ?



Sol.

4. Which of the following species expected to have maximum enthalpy in an electrophilic aromatic substitution reaction ?

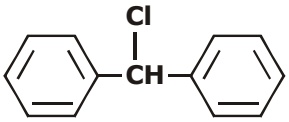


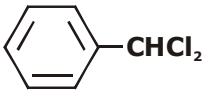
(A) Species (II) (B) Species (III)

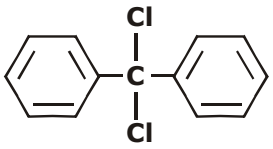
(C) Species (IV) (D) Species (V)

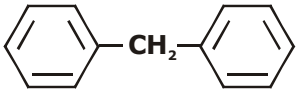
Sol.

5. Which of the following structures correspond to the product expected, when excess of C_6H_6 reacts with CH_2Cl_2 in presence of anhydrous $AlCl_3$?

(A) 

(B) 

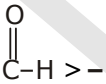
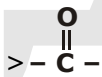
(C) 

(D) 

Sol.

6. Conjugation of electron withdrawing groups,

e.g., –CHO,  ,  , –C ≡ N, –NO_2 activates nucleophilic attack in halobenzene. The order of reactivity of these group towards nucleophilic aromatic substitution.

(A) –NO_2 > –C ≡ N >  >  > 

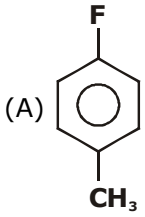
(B)  >  > > –C ≡ N > –NO_2

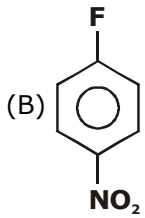
(C) –C ≡ N > –NO_2 >  >  > 

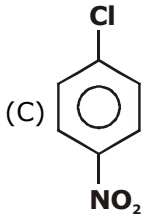
(D) > –NO_2 > –C ≡ N >  >

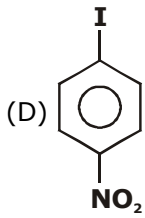
Sol.

7. Which of most reactive towards nucleophilic aromatic substitution.

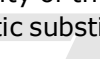
(A) 

(B) 

(C) 

(D) 

Sol.

8. **Statement-1 :** Nitro benzene reacts with  , $AlCl_3$ to produce m-nitroacetophenone.

Statement-2 : NO_2 group attached to the ring is a meta directing during S_E.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT correct explanation for statement-1

(C) Statement-1 is true, statement-2 is false

(D) Statement-1 is false, statement-2 is true

Sol.

9. **Statement-1 :** Rate of nitration is $C_6H_6 \simeq C_6D_6 \simeq C_6T_6$

Statement-2 : Formation of wheland intermediate is rate determining step in nitration of benzene, not the breaking of C–H or C–D bond.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1

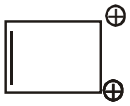
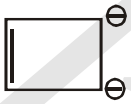
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT correct explanation for statement-1

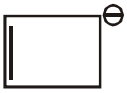
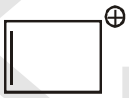
(C) Statement-1 is true, statement-2 is false

(D) Statement-1 is false, statement-2 is true

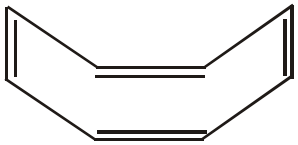
Sol.

10.  $\xrightarrow{2Na}$ (A) Product (A) is

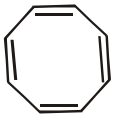
(A)  (B) 

(C)  (D) 

Sol.

11.  $\xrightarrow[\Delta]{2Na}$ (A) Product

(A) is

(A)  (B) 

(C) 

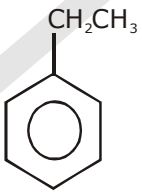
(D) All

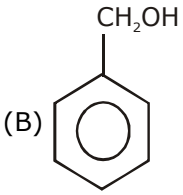
Sol.

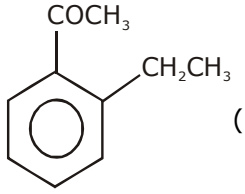
12. Which aromatic compound is obtained when n - octane undergoes catalytic hydroforming (Aromatization) on heating with $Al_2O_3 + Cr_2O_3$.
(A) ethyl benzene (B) m-Xylene
(C) o-Xylene
(D) p-Xylene

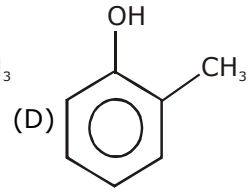
Sol.

13. Benzoic acid may be prepared by the oxidation of:

(A) 

(B) 

(C) 

(D) 

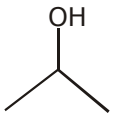
Sol.

14. Isopropylbenzene can be prepared by :

(A) Benzene + $CH_3CH = CH_2 \xrightarrow{H_2SO_4}$

(B) Benzene + $CH_3 - \underset{\underset{Cl}{|}}{CH} - CH_3 \xrightarrow{AlCl_3}$

(C) Benzene +  $\xrightarrow{AlCl_3}$

(D) Benzene +  $\xrightarrow{H^\oplus}$

Sol.

15. In which of the following reaction t-butylbenzene is formed:

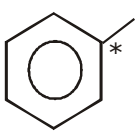
(A) Benzene + iso-butyl chloride, $AlCl_3$

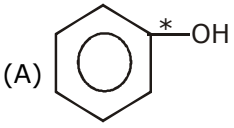
(B) Benzene + $(CH_3)_2C = CH_2 \xrightarrow{BF_3.HF}$

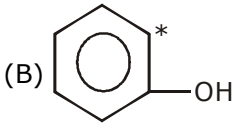
(C) Benzene + t-butyl alcohol $\xrightarrow{H_2SO_4}$

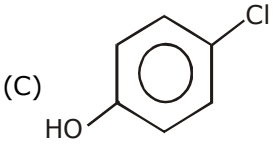
(D) Benzene + $(CH_3)_2C = CH_2 \xrightarrow{H^\oplus}$

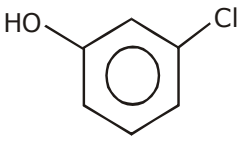
Sol.

16.  $\xrightarrow[395^\circ C]{NaOH\ \ H_2O}$ Product is:

(A) 

(B) 

(C) 

(D) 

Sol.

17. Which of the following reactions of bezene proves the presence of three carbon - carbon double bonds in it:

(A) Formation of a triozonide

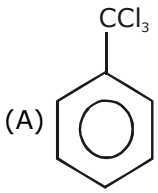
(B) Hydrogenation of bezene to cyclohexane

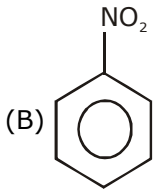
(C) Formation of $C_6H_6Cl_6$ by addition of chlorine

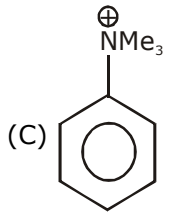
(D) Formation of nitrobenzene on heating benzene with a mixture of concentrated nitirc acid and sulphuric acid

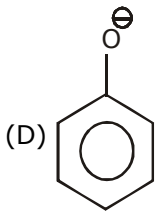
Sol.

18. Electrophile $NO_2^\oplus$ attacks the following in which cases $NO_2^\oplus$ will be at meta position:

(A) 

(B) 

(C) 

(D) 

Sol.

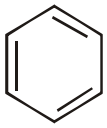
19. The reaction of replacement of a hydrogen atom in benzene by alkyl group can be brought about with the following reagents:
(A) Alkyl chloride and $AlCl_3$
(B) Alkene and BF_3,HF
(C) Alkanol and alkali
(D) Alkanol and acid

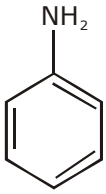
Sol.

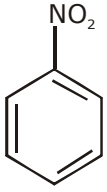
20. Which of the following statements is correct:
(A) Bromination of toluene occurs faster than that of benzene
(B) Nitration of toluene is faster than that of ethylbenzene
(C) The bromonium ion is a good nucleophile
(D) Effective nitrating agent is nitrate ion

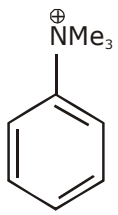
Sol.

21. Which of the following gives Friedel Crafts reaction?

(A) 

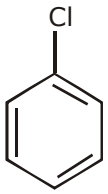
(B) 

(C) 

(D) 

Sol.

22. Which of the following can be used in Friedel Crafts reaction when benzene used with $AlCl_3$

(A) 

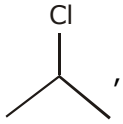
(B) $CH_2 = CH - Cl$

(C) CH_3CH_2Cl

(D) $CH_2= CH–CH_2–Cl$

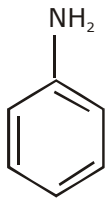
Sol.

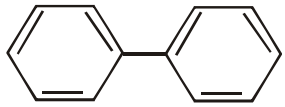
23. The good method for converting benzene into n-propyl benzene is:
(A) $C_6H_6 + CH_3CH_2CH_3Cl$ + Anhyd.$AlCl_3$
(B) $C_6H_6 + CH_3CH_2COCl$ + Anhyd. $AlCl_3$ and then treatment with Zn/Hg/HCl
(C) $C_6H_6 + CH_3CH_2COCl$ + Anhyd. $AlCl_3$ and then treatment with H_2Ni

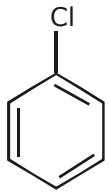
(D) C_6H_6 +  , $AlCl_3$

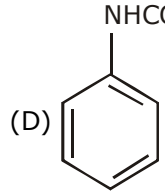
Sol.

24. Which of the following will undergo nitration slower than benzene ?

(A) 

(B) 

(C) 

(D) 

Sol.

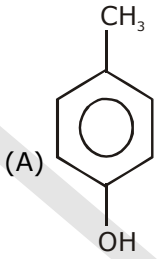
25. Which of the following is ortho-para directing group

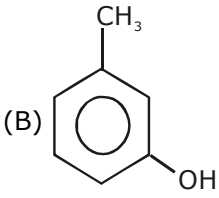
(A) CF_3 (B) CCl_3

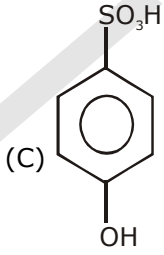
(C) – CH = CH – COOH (D) – N ≡ C

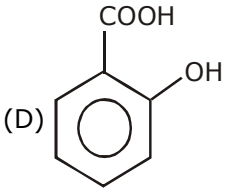
Sol.

26. The structure of the compound that gives a tribromo derivative on treatment with bromine water is:

(A) 

(B) 

(C) 

(D) 

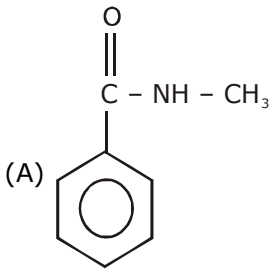
Sol.

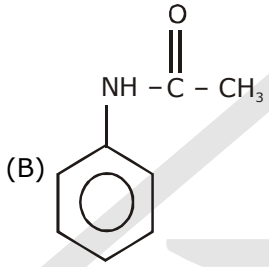
27. Amongst the following the moderately activating group is-

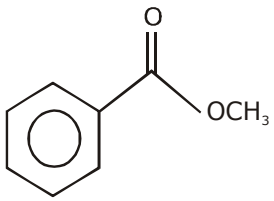
(A) – NHR (B) – $NHCOCH_3$
(C) – NR_2 (D) – CH_3

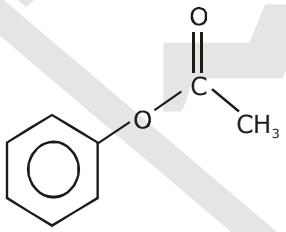
Sol.

28. Which of the following is ortho para directing

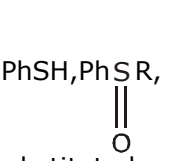
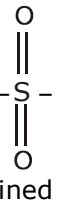
(A) 

(B) 

(C) 

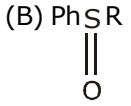
(D) 

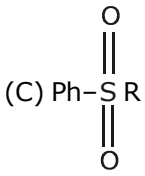
Sol.

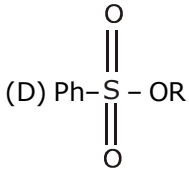
29. Of the species PhSH,  and 

OR the meta- substituted product is obtained from

(A) PhSR

(B) 

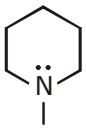
(C) 

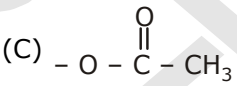
(D) 

Sol.

30. Which of the following group(s) activate the benzene ring towards electrophilic substitution reaction.

(A) –Cl

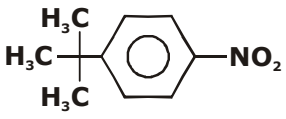
(B) 

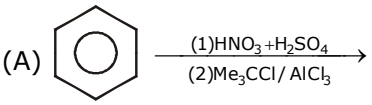
(C) 

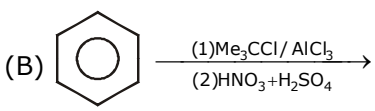
(D) $-C\equiv\ddot{N}$

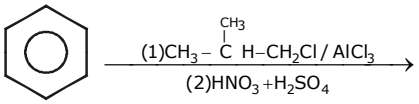
Sol.

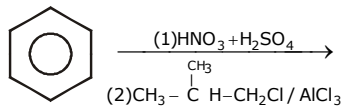
31. Choose the best method to prepare given compound :



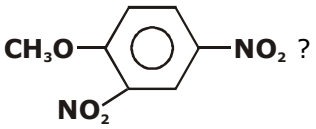
(A) 

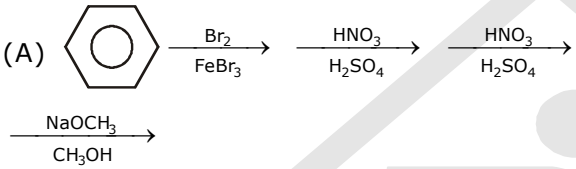
(B) 

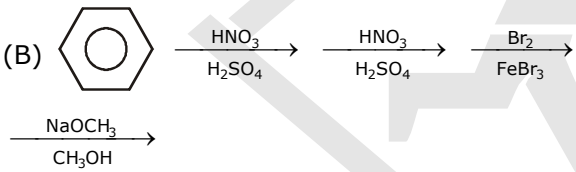
(C) 

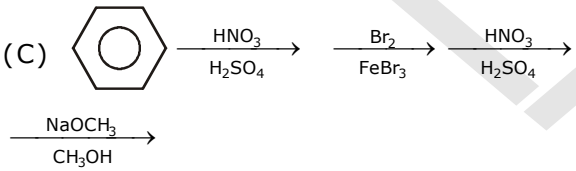
(D) 

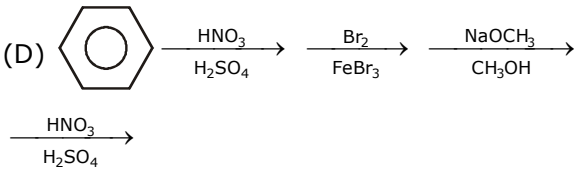
Sol.

32. Which is the best synthesis of 

(A) 

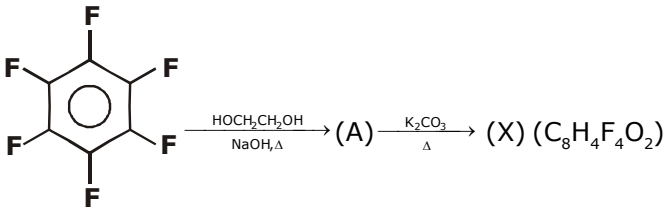
(B) 

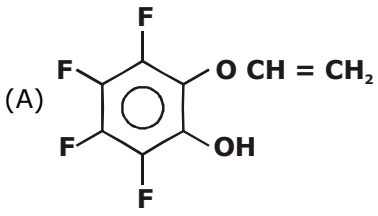
(C) 

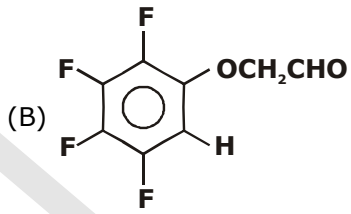
(D) 

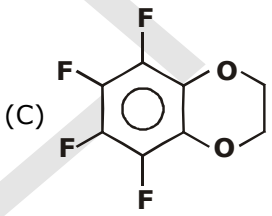
Sol.

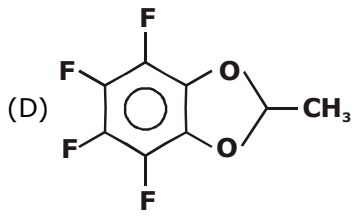
33. The cumulative effect of their fluorine activate the rings of penta and hexa fluorobenzene toward nucleophilic aromatic substituiton. What is compound X in the following synthesis ?



(A) 

(B) 

(C) 

(D) 

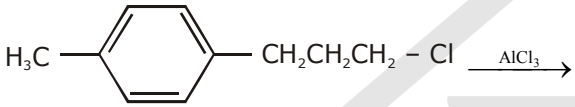
Sol.

EXERCISE – III SUBJECTIVE PROBLEMS (JEE ADVANCED)

1. What product is formed when 2-methylpropene is added to a large excess of benzene containing HF and the Lewis acid BF_3? By what mechanism is it formed?

Sol.

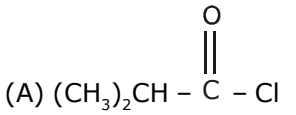
2. Predict the product of the following reaction and give the curved-arrow mechanism for its formation. (Hint: Friedel-Crafts alkylations can be used to form rings.)

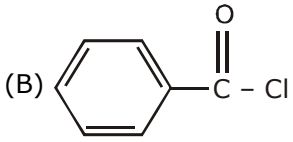


(a compound $C_{10}H_{12}$+HCl)

Sol.

3. Give the structure of the product expected from the reaction of each of the following compounds with benzene in the presence of one equivalent of $AlCl_3$, followed by treatment with water.



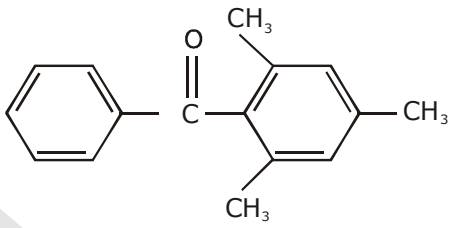


Isobutyryl chloride

benzoyl chloride

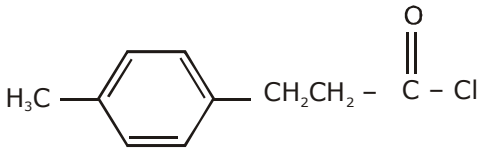
Sol.

4. Show two different Friedel-Crafts acylation reactions that can be used to prepare the following compound.



Sol.

5. The following compound reacts with $AlCl_3$ followed by water to give a ketone A with the formula $C_{10}H_{10}O$. Give the structure of A and a curved -arrow mechanism for its formation

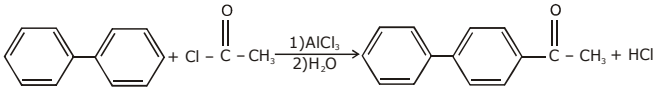


Sol.

6. Predict the product(s) of
(A) Friedel-Crafts acylation of anisole (methoxybenzene) with acetyl chloride in the presence of one equivalent of $AlCl_3$ follwed by H_2O.
(B) Friedel-Crafts alkylation of a large excess of ethylbenzene with chloromethane in the presence of $AlCl_3$.

Sol.

7. Biphenyl (phenylbenzene) undergoes the Friedel-Crafts acylation reaction, as shown by the follwoing example.

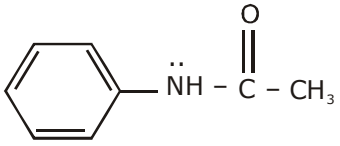


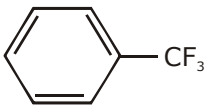
biphenyl

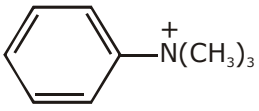
p-phenylacetophenone
On the basis of this result, what is the directing effect of the phenyl group ?

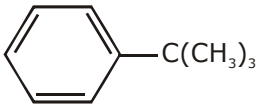
Sol.

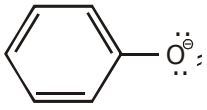
8. Predict the predominant products that would result from bromination of each of the following compounds. Classify each substituent group as an ortho, para director or a meta director. and explain your reasoning

(A) 

(B) 

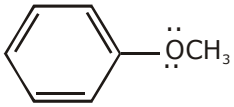
(C) 

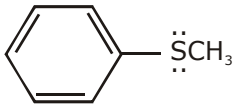
(D) 

(E) 

Sol.

9. Explain why the nitration of anisole is much faster than the nitration of thioanisole under the same conditions.

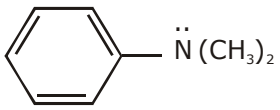




anisole thioanisole

Sol.

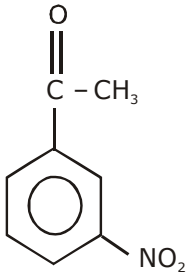
10. Which should be faster bromination of benzene or bromination of N,N - dimethylaniline? Explain your answer carefully.



N,N - dimethylaniline

Sol.

11. Outline a synthesis of m-nitroacetophenone from benzene: explain your reasoning.



Sol.

12. Give the products expected(if any) when ethylbenzene reacts under the following conditions.
(A) Br_2 in CCl_4 (dark)
(B) HNO_3 ,H_2SO_4
(C) conc. H_2SO_4

(D) $C_2H_5 - C - Cl, AlCl_3$(1.1 equiv.) then H_2O

(E) $CH_3Br, AlCl_3$
(F) $Br_2, FeBr_3$

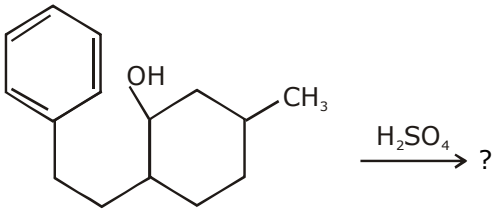
Sol.

13. Give the products expected (if any) when nitrobenzene reacts under the following conditions.
(A) $Cl_2, FeCl_3$, heat
(B) fuming HNO_3, H_2SO_4

(C) $H_3C - C - Cl, AlCl_3$(1.1 equiv.) then H_2O

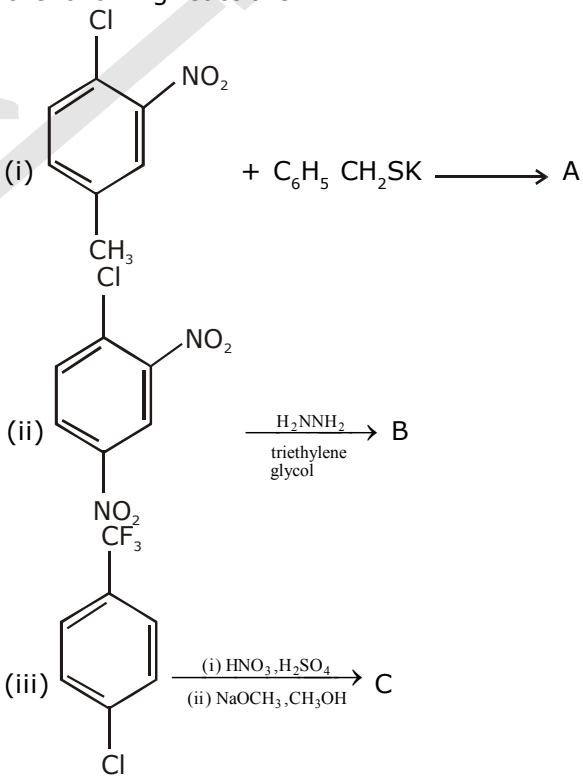
Sol.

14. When the following compound is treated with H_2SO_4 the product of the resulting reaction has the formula $C_{15}H_{20}$ and does decolorize Br_2 in CCl_4. Suggest a structure for this product and give a curved - arrow mechanism for its formation.



Sol.

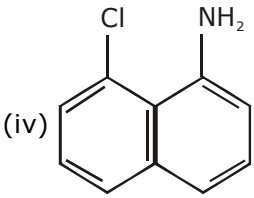
15. Write the principal organic product in each of the following reactions:

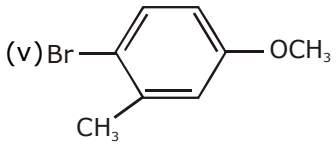


(i) + $C_6H_5\ CH_2SK$ ⟶ A

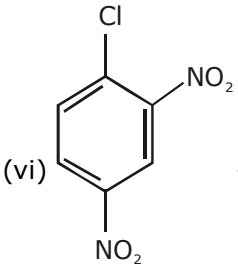
(ii) $\xrightarrow[\text{triethylene glycol}]{H_2NNH_2}$ B

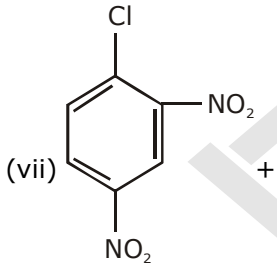
(iii) $\xrightarrow[(ii)\ NaOCH_3, CH_3OH]{(i)\ HNO_3, H_2SO_4}$ C

(iv)  $\xrightarrow[\text{(ii) CuBr}]{\text{(i) } NaNO_2, HBr}$ D

(v) 

$\xrightarrow[\text{(ii) } NaSCH_3]{\text{(i) NBS, Benzoylperoxide, } CCl_4 \text{ .heat}}$ E

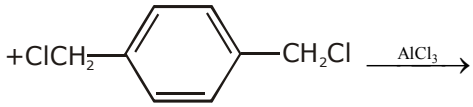
(vi)  $+ CH_3CH_2ONa \longrightarrow F$

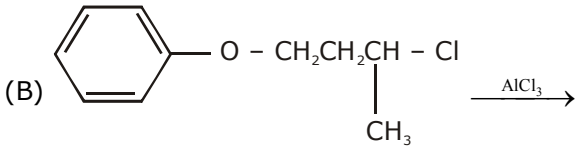
(vii)  $+ C_6H_5CH_2SNa \longrightarrow G$

Sol.

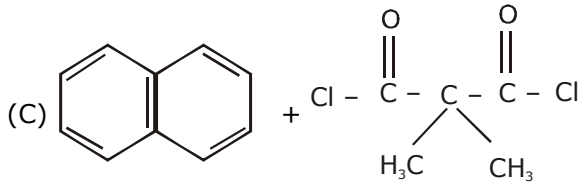
16. Complete the following reactions?

(A) benzene (large excess)

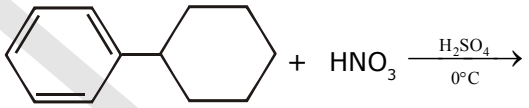


(B) 

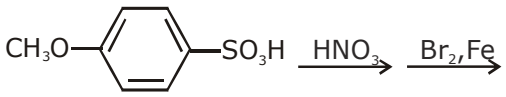
(a compound with ten carbons)

(C) 

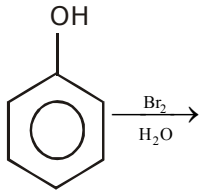
$\xrightarrow[\text{2) } H_2O]{\text{1) } AlCl_3}$ (three products, all naphthalene -dimethylmalonyl dichloride isomers with formula $C_{15}H_{12}O_2$)

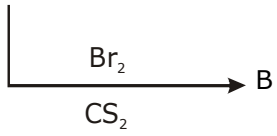
(D) 

(E) ferrocene + $H_3C-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[\text{2) } H_2O]{\text{1) } AlCl_3}$ ($C_{12}H_{12}OFe$)

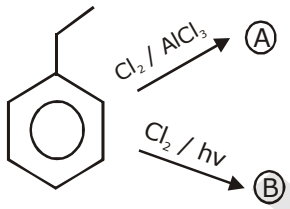
(F) 

Sol.

17.  Product A and B is



Sol.

18. 

Product A and B is

Sol.

Match the following

19. Substituent on phenyl ring.

(A) $-CH_2-CH_3$ (P) o/p - directors

(B) $-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-CH_3$ (Q) meta directors

(C) $-NH-\overset{\overset{O}{\|}}{C}-CH_3$ (R) Activating group

(D) $-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-CH_3$ (S) Deactivating group

Sol.

20. **Column I**

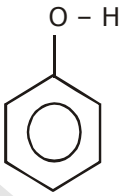
(A) CO_2 is evolved from

(B) Libbermann nitroso test is given by

(C) Compounds gives yellow oily

(D) When reacts with $\xrightarrow[HO^{\ominus}]{CHCl_3}$

Column II

(P) 

$NaHCO_3$ by the reaction of

(Q) 

(R) R – NH – R

liquid on reaction with $NaNO_2 + HCl$

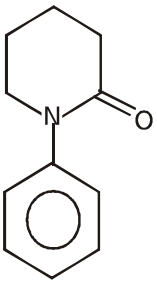
(S) Ph $-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-$ OH

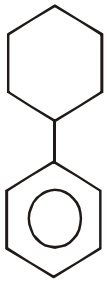
salicy ladehyde will form

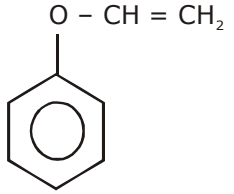
Sol.

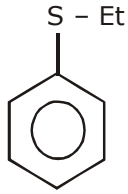
21. Compounds

Substituent on phenyl

(A)  (P) Activating group

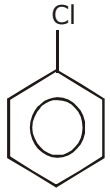
(B)  (Q) Deactivating group

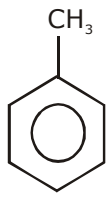
(C)  (R) o/p director

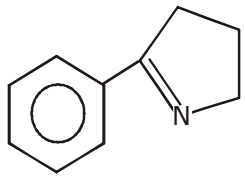
(D)  (S) meta- director

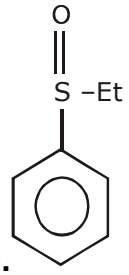
Sol.

22. **Column I** **Column II**

(A)  (P) Group attached to benzene ring is a + M group here

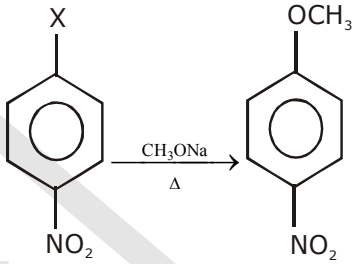
(B)  (Q) Group attached to benzene ring is a – M group here

(C)  (R) Electropile would attack on ortho or para position

(D)  (S) Rate of electrophilic substitution is less than that of bnzene

Sol.

23. Match th column :



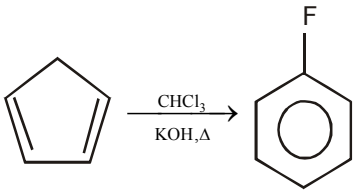
X = halogen

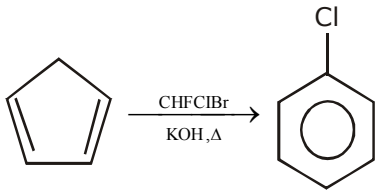
relative reactivity toward (SNAr)

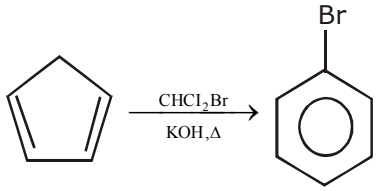
(A)– F	(P) 312
(B) – Cl	(Q) 1
(C) – Br	(R) 0.8
(D) – I	(S) – 1

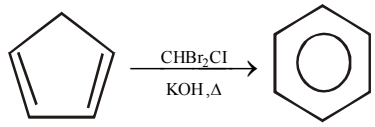
Sol.

24. Matrix : Reaction Product

(A) 

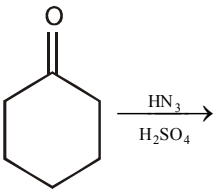
(B) 

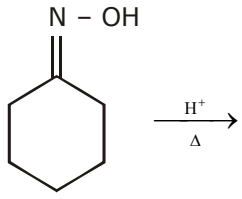
(C) 

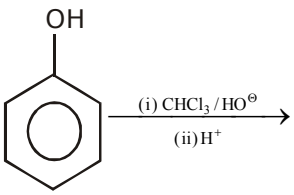
(D) 

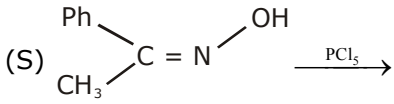
Sol.

25. **Column-I**
(A) Caprolactum formation take place in
(B) Beckmann rearrangement is
(C) Schmidt reaction is
(D) Reaction in which number of
Column-II

(P) 

(Q) 

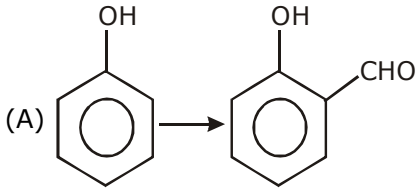
(R) 

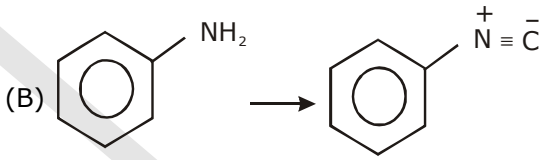
(S) 

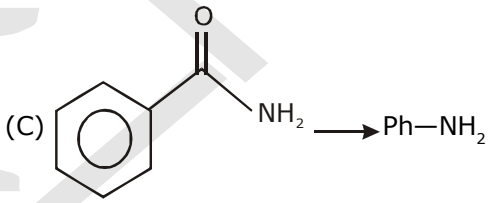
carbon increases

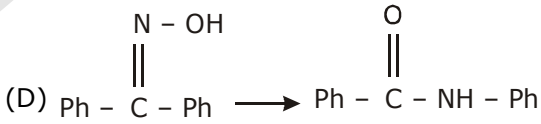
Sol.

26. Column-I Column-II (Reagent used)

(A) 

(B) 

(C) 

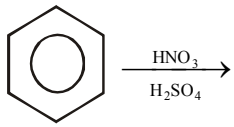
(D) 

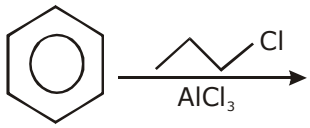
Column-II
(P) $CHCl_3$ / KOH
(Q) Br_2 / KOH
(R) H_2SO_4
(S) PCl_5

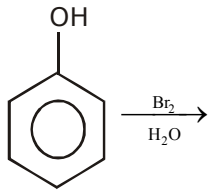
Sol.

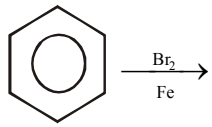
27. Matrix

Column-I

(A) 

(B) 

(C) 

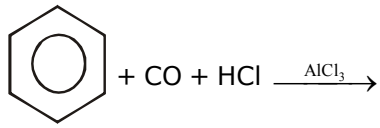
(D) 

Column - II

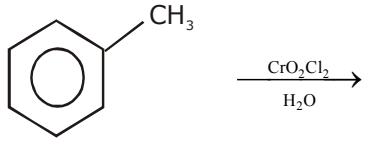
(P) Carbocation is intermediate
(Q) Carabanion is intermediate
(R) Electrophilic substitution reaction
(S) Rearrangement takes place

Sol.

28. **Column-I**

(A) 

(B) Ph – C = N $\xrightarrow[H_2O]{SnCl_2/HCl}$

(C) 

(D) Ph – C ≡ N $\xrightarrow{H_3O^{\oplus}}$

Column-II

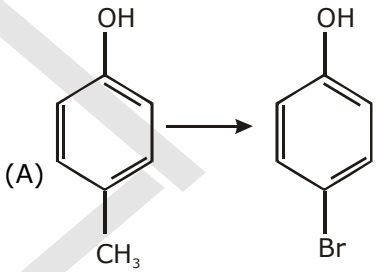
(P) Ph – CHO is product
(Q) Etard reaction
(R) Stephon reduction
(S) Gattermann Koch reaction
(T) Ph – CO_2H

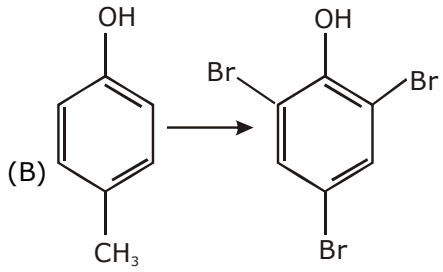
Sol.

Comprehension - 3 (29 to 31)

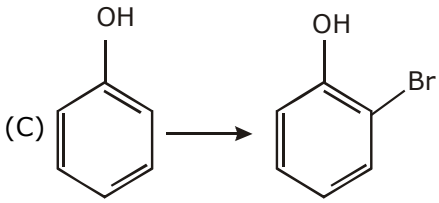
It is not always easy to predict the position of attack on multiply substituted benzene. If the benzene ring bears different group ortho/ para directing group at the 1 and 4 positions, the position of further substitution is not immediately clear.

29. Which of the following synthesis could be done in the single step ?

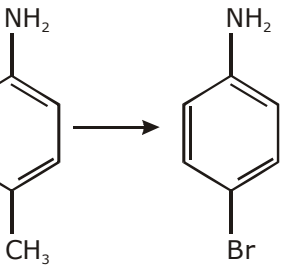
(A) 



(B)

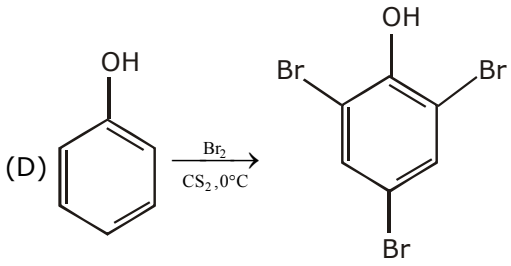
(C) 

(D)



Sol.

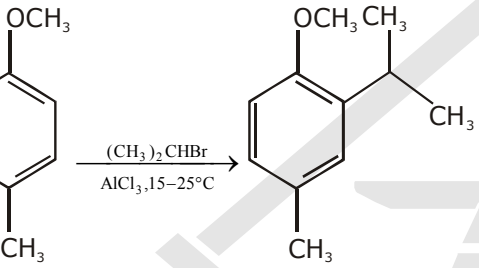
(D)



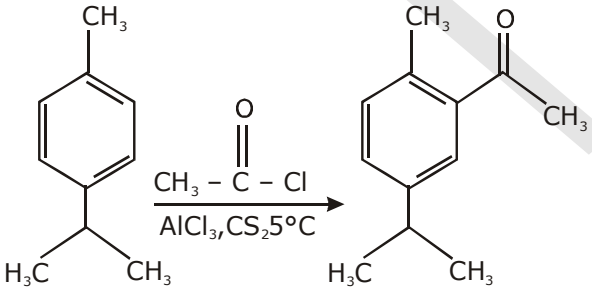
Sol.

30. Which of following is the incorrect major product ?

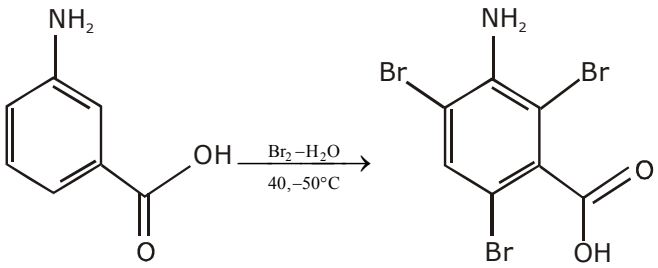
(A)



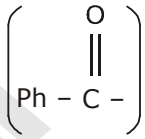
(B)

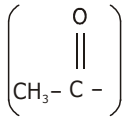


(C)



31. Which of the following side chain reaction/s can be used to reduce the activity of strongly activating groups like – OH

(A) benzoylation 

(B) acetylation 

(C) both of the above

(D) none of the above

Sol.

EXERCISE – IV PREVIOUS YEARS PROBLEMS

LEVEL – I JEE MAIN

Q.1 Fluorobenzene (C_6H_5F) can be synthesized in the laboratory - **[AIEEE 2006]**

(A) from aniline by diazotisation followed by heating the diazonium salt with HBF_4

(B) by direct fluorination of benzene with F_2 gas

(C) by reacting bromobenzene with NaF solution

(D) by heating phenol with HF and KF

Sol.

Q.2 Phenyl magnesium bromide reacts with methanol to give - **[AIEEE 2006]**

(A) a mixture of benzene and Mg(OMe) Br

(B) a mixture of toluene and Mg(OH)Br

(C) a mixture of phenol and Mg(Me)Br

(D) a mixture of anisole and Mg(OH) Br

Sol.

Q.3 The reaction of toluene with Cl_2 in presence of $FeCl_3$ gives predominantly - **[AIEEE 2007]**

(A) benzoyl chloride

(B) benzyl chloride

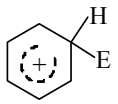
(C) o-and p-chlorotoluene

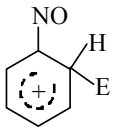
(D) m-chlorotoluene

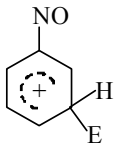
Sol.

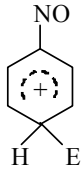
Q.4 The electrophile, $E^{\oplus}$ attacks the benzene ring to generate the intermediate σ-complex. Of the following, which σ-complex is of lowest energy ?

[AIEEE 2008]

(A) 

(B) 

(C) 

(D) 

Sol.

Q.5 Toluene is nitrated and the resulting product is reduced with tin and hydrochloric acid. The product so obtained is diazotised and then heated with cuprous bromide. The reaction mixture so formed contains - **[AIEEE 2008]**

(A) mixture of o– and p-dibromobenzenes

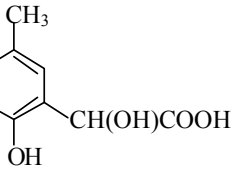
(B) mixture of o- and p-bromoanilines

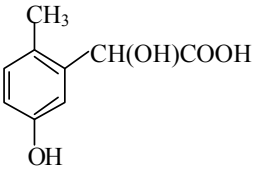
(C) mixture of o- and m-bromotoluenes

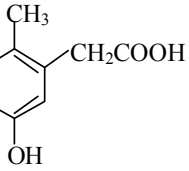
(D) mixture of o- and p-bromotoluenes

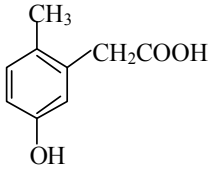
Sol.

Q.6 p–cresol reacts with chloroform in alkaline medium to give the compound A which adds hydrogen cyanide to form, the compound. B The latter on acidic hydrolysis gives chiral carboxylic acid. The structure of the carboxylic acid is - **[AIEEE-2005]**

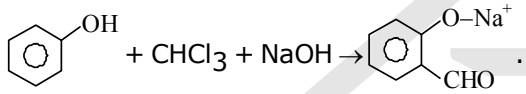
(A) 

(B) 

(C) 

(D) 

Sol.

Q.7  .

The electrophile involved in the above reaction is : **[AIEEE 2006]**

(A) dichlorocarbene ($:CCl_2$)

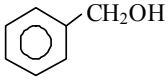
(B) trichloromethyl anion ($\overset{\ominus}{C}Cl_3$)

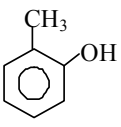
(C) formyl cation ($\overset{\oplus}{C}HO$)

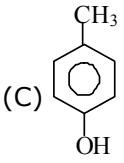
(D) dichloromethyl cation ($\overset{+}{C}HCl_2$)

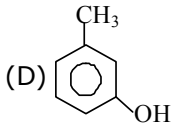
Sol.

Q.8 The structure of the compound that gives a tribromo derivative on treatment with bromine water is - **[AIEEE 2006]**

(A) 

(B) 

(C) 

(D) 

Sol.

Q.9 Phenol, when it first reacts with concentrated sulphuric acid and then with concentrated nitric acid, gives - **[AIEEE 2008]**

(A) o-nitrophenol

(B) p-nitrophenol

(C) nitrobenzene

(D) 2, 4, 6-trinitrobenzene

Sol.

Q.10 The major product obtained on interaction of phenol with sodium hydroxide and carbon dioxide is - **[AIEEE 2009]**

(A) salicylaldehyde (B) salicyclic acid

(C) phthalic acid (D) benzoic acid

Sol.

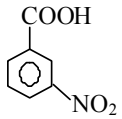
Q.11 Which one of the following undergoes reaction with 50% sodium hydroxide solution to give the corresponding alcohol and acid ? **[AIEEE-2004]**

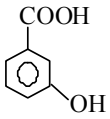
(A) Phenol (B) Benzaldehyde

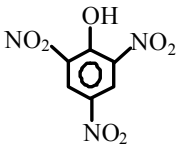
(C) Butanal (D) Benzoic acid

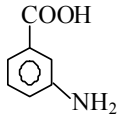
Sol.

Q.12 Picric acid is – **[AIEEE-2002]**

(A) 

(B) 

(C) 

(D) 

Sol.

Q.13 Consider the acidity of the carboxylic acids : **[AIEEE-2004]**

(a) PhCOOH
(b) o – $NO_2C_6H_4COOH$
(c) p – $NO_2C_6H_4COOH$
(d) m – $NO_2C_6H_4COOH$
Which of the following order is correct ?
(A) a > b > c > d (B) b > d > c > a
(C) b > d > a > c (D) b > c > d > a

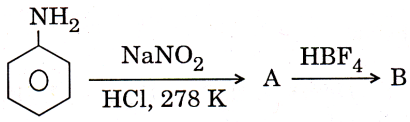
Sol.

Q.14 The compound formed as a result of oxidation of ethyl benzene by $KMnO_4$ is – **[AIEEE-2007]**

(A) benzophenone (B) acetophenone
(C) benzoic acid (D) benzyl alcohol

Sol.

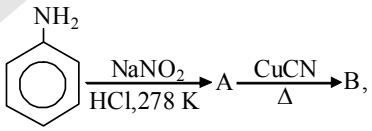
Q.15 In the chemical reactions. **[AIEEE-2010]**



The compounds 'A' and 'B' respectively are
(A) nitrobenzene and chlorobenzene
(B) nitrobenzene and flurobenzene
(C) phenol and benzene
(D) benzene diazonium chloride and flurobenzene

Sol.

Q.16 In the chemical reactions **[AIEEE-2011]**



the compounds A and B respectively are :
(A) Benzene diazonium chloride and benzonitrit
(B) Nitrobenzene and chlorobenzene
(C) Phenol and bromobenzene
(D) Fluorobenzene and phenol

Sol.

LEVEL – II

JEE ADVANCED

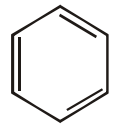
1. Statement -1 Phenol is more reactive than benzene towards electrophilic substitution reaction.
Statement -2 In the case of phenol the intermediate carboation is more resonance stabilized.
(A) Statement -1 is true Statement -2 is true and Statement -2 is correct explanation for Statement -1
(B) Statement -1 is true Statement -2 is true and Statement -2 is not correct explanation for Statement -1
(C) Statement -1 is true Statement -2 is false
(D) Statement -1 is false Statement -2 is true
[JEE 2000]

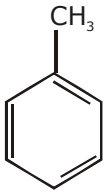
Sol.

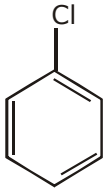
2. Amongst the following the strongest base is
[JEE 2000]
(A) $C_6H_5NH_2$ (B) p-$O_2NC_6H_4NH_2$
(C) m-$O_2NC_6H_4NH_2$ (D) $C_6H_5CH_2NH_2$

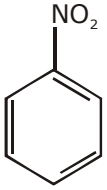
Sol.

3. Identify the correct order of reactivity in electrophilic substitution reactions of the following compunds : **[JEE 2002]**

(I) 

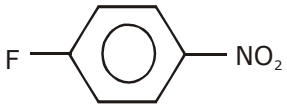
(II) 

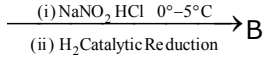
(III) 

(IV) 

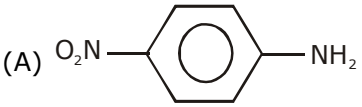
(A) I>II>III>IV (B) IV>III>II>I
(C) II>I>III>IV (D) II>III>I>IV

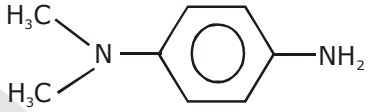
Sol.

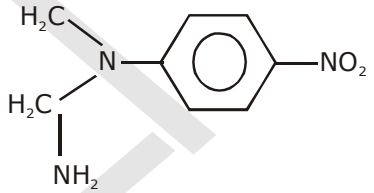
4. 

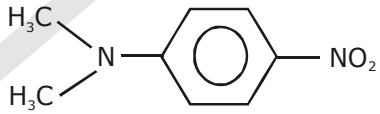


[JEE 2003]

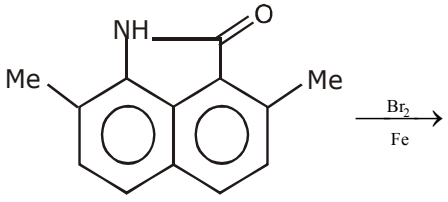
(A) 

(B) 

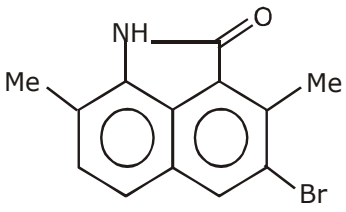
(C) 

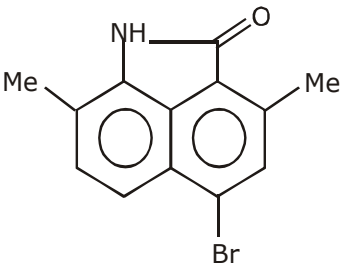
(D) 

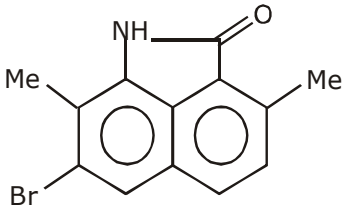
Sol.

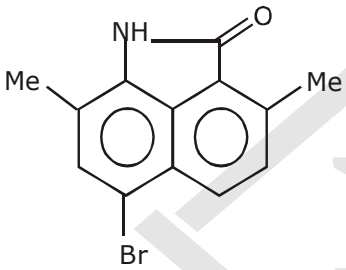
5. 

Major product of above reaction is:
[JEE 2004]

(A) 

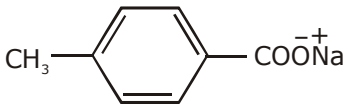
(B) 

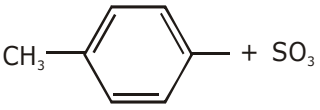
(C) 

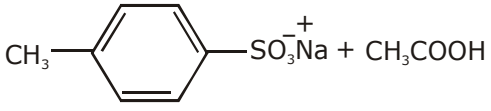
(D) 

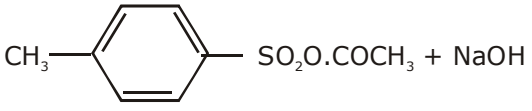
Sol.

6. Which of the following is obtained when 4-Methylbenzenesulphonic acid is hydrolysed with excess of sodium acetate ? **[JEE 2005]**

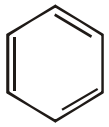
(A) 

(B) 

(C) 

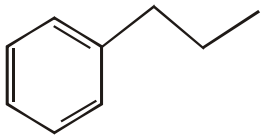
(D) 

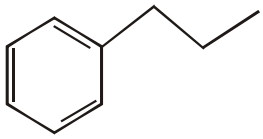
Sol.

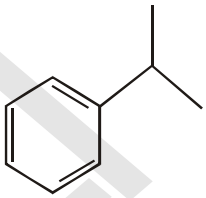
7.  + Cl – CH_2CH_2 – CH_3 $\xrightarrow{AlCl_3}$ P

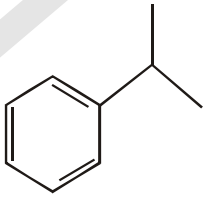
$\xrightarrow[(ii)\,H_3O^+]{(i)\,O_2/\Delta}$ Q + Phenol P and Q are respectively

[JEE 2006]

(A)  + CH_3CH_2CHO

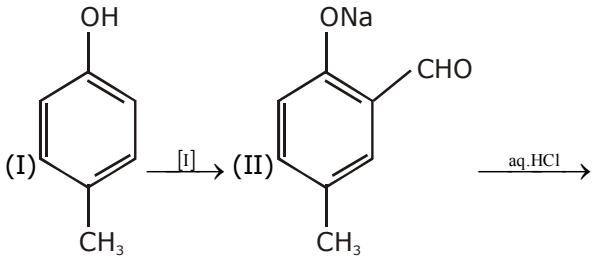
(B)  + CH_3COCH_3

(C)  + CH_3COCH_3

(D)  + CH_3CH_2CHO

Sol.

Comprehension Type : (Q.8 to Q.10)
Reimer -Tiemann reaction introduces an aldehyde group on to the aromatic ring of phenol, ortho to the hydroxyl group. This reaction involves electrophilic aromatic substitution. This is a general method for the synthesis of substituted salicyladehydes as depicted below. **[JEE 2007]**



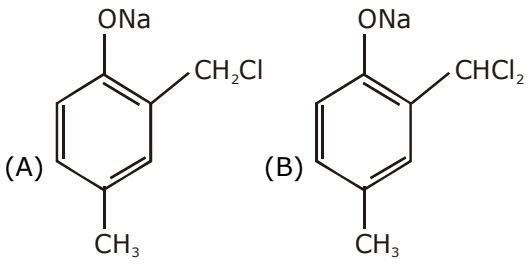
8. Which one of the following reagents is used in the above reaction?
(A) aq NaOH + CH_3Cl
(B) aq NaOH + CH_2Cl_2
(C) aq NaOH + $CHCl_3$
(D) aq NaOH + CCl_4

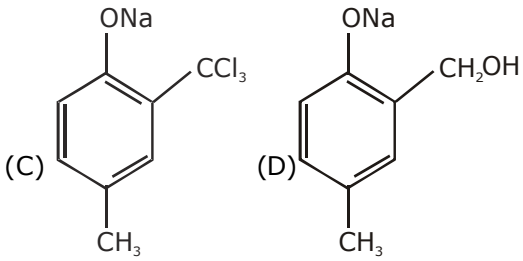
Sol.

9. The electrophile in this reaction is
(A) :CHCl (B) $\overset{\oplus}{C}HCl_2$
(C) $:CCl_2$ (D) $\dot{C}Cl_3$

Sol.

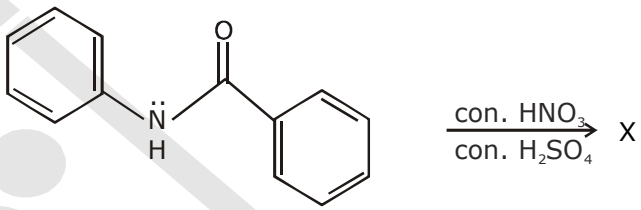
10. The structure of the intermediate I is



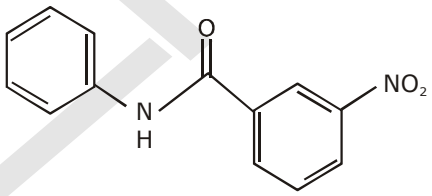


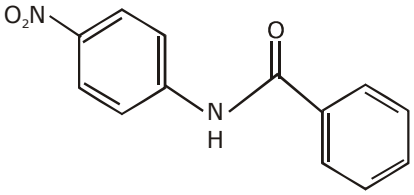
Sol.

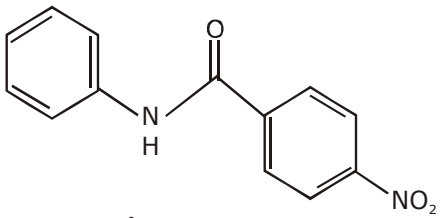
11. In the following reaction

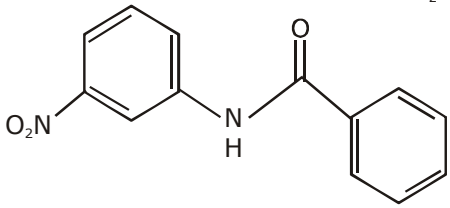


the structure of the major product 'X' is

(A) 

(B) 

(C) 

(D) 

Sol.

12. Statement-1: p- Hydroxybenzoic acid has a lower boiling point than o- hydroxybenzoic acid. **[JEE 2007]**
Statement-2: o-Hydroxybenzoic acid has intramolecular hydrogen bonding.
(A) Statement-1 is True Statement-2 is True Statement-2 is a correct explanation for Statement-1
(B) Statement-1 is True Statement-2 is True Statement-2 is Not explanation for Statement-1
(C) Statement-1 is True Statement-2 is False
(D) Statement-1 is False Statement-2 is True

Sol.

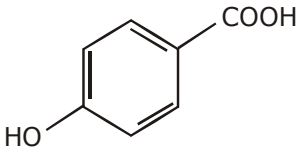
13. Statement-1: Bromobenzene upon reaction with Br_2 / Fe gives 1,4-dibromobenzene as the major product. **[JEE 2008]**
Statement-2: in bromobenzene the inductive effect of the bromo group is more dominant than the mesomeric effect in directing the incoming electrophile.
(A) Statement-1 is True Statement-2 is True Statement-2 is a correct explanation for Statement-1
(B) Statement-1 is True Statement-2 is True Statement-2 is Not explanation for Statement-1
(C) Statement-1 is True Statement-2 is False
(D) Statement-1 is False Statement-2 is True

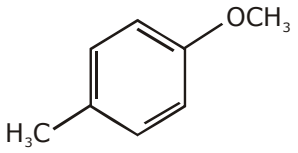
Sol.

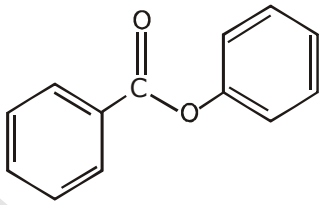
14. Statement-1 : Aniline on reaction with $NaNO_2$ /HCl at 0°C followed by coupling with β - naphthol gives a dark blue coloured precipitate. **[JEE 2008]**
Statement-2 : The colour of the compound formed in the reaction of aniline with $NaNO_2$ / HCl at 0° followed by coupling with β naphthol is due to the extended conjugation.
(A) Statement-1 is True Statement-2 is True Statement-2 is a correct explanation for Statement-1
(B) Statement-1 is True Statement-2 is True Statement-2 is Not explanation for Statement-1
(C) Statement-1 is True Statement-2 is False
(D) Statement-1 is False Statement-2 is True

Sol.

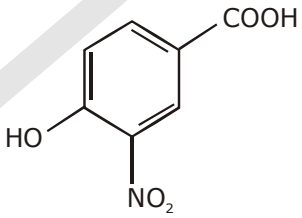
15. The compounds P,Q and S **[JEE 2010]**

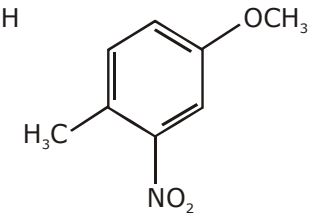
(P) 

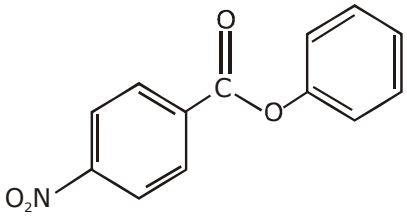
(Q) 

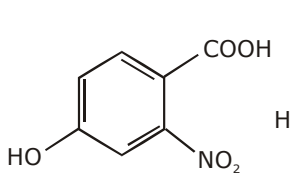
(S) 

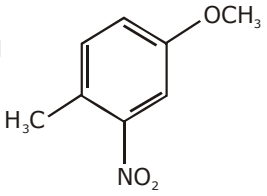
were separately subjected to nitration using HNO_3 / H_2SO_4 mixture.The major product formed in each case respectively is

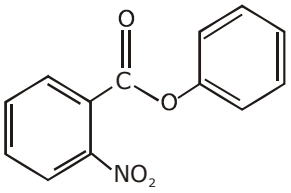
(A) 

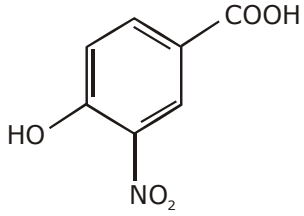


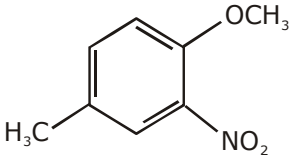


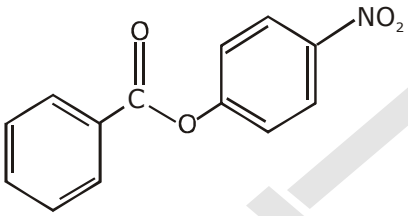
(B) 

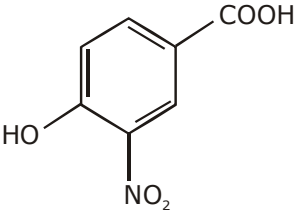


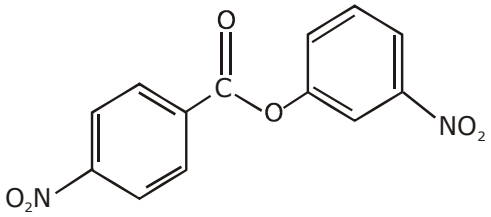


(C) 



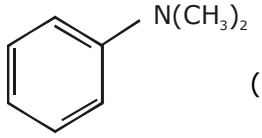


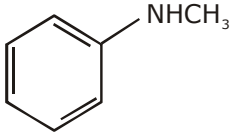
(D) 

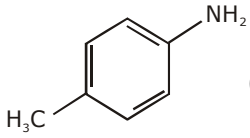


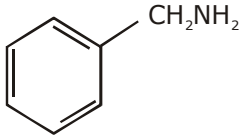
Sol.

16. Amongst the compounds given the one the would form a brilliant colored dye on treatment with $NaNO_2$ in dil. HCl followed by addition to an alkaline solution of β - naphthol is **[JEE 2011]**

(A) 

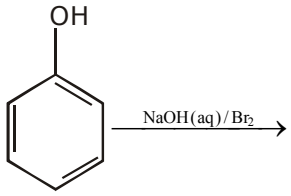
(B) 

(C) 

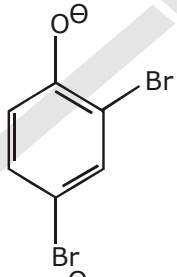
(D) 

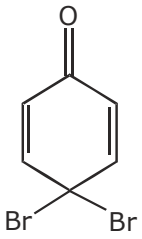
Multiple Choice Question:

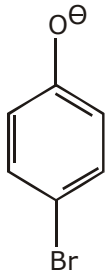
Sol.

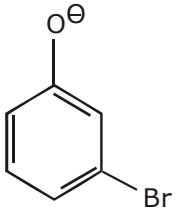
17. In the reaction 

the intermediate (s) is (are) **[JEE 2010]**

(A) 

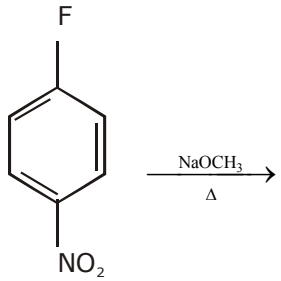
(B) 

(C) 

(D) 

Sol.

18. What would be the major product in the following reaction? **[JEE 2000]**

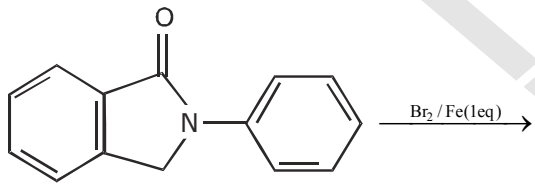


Sol.

19. How would you bring about the following conversion (in 3 steps)? **[JEE 2000]**
Aniline $\rightarrow$ Benzylamine

Sol.

20. What would be the major product in the following reaction ? **[JEE 2000]**



Sol.

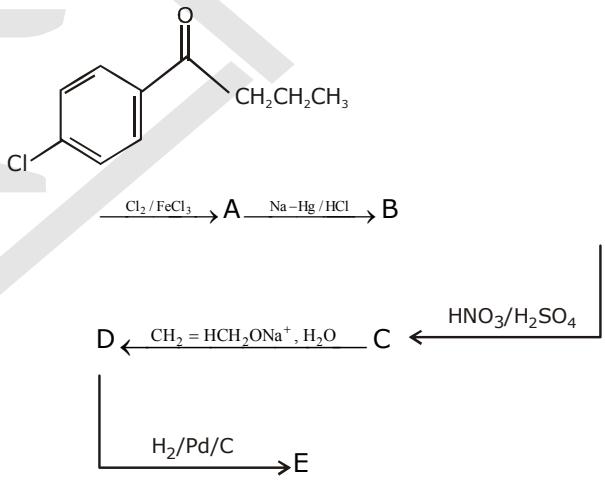
21. Give reasons for the following: **[JEE 2000]**
(i) tert-butylbenzene does not give benzoic acid on treatment with acidic $KMnO_4$
(ii) Normally benzene gives electrophilic substitution reaction rather than electrophilic addition reaction although it has double bond.

Sol.

22. How would you synthesis 4 methoxyphenol from bromobenzene in NOT more than five steps? State clearly the reagents used in each step and show the structures of the intermediate compounds in your synthetic scheme. **[JEE 2001]**

Sol.

23. Write structures of the products A,B,C D and E in the following scheme **[JEE 2002]**



Sol.

24. Carry out the following conversions. **[JEE 2003]**

(i) Phenol to aspirin

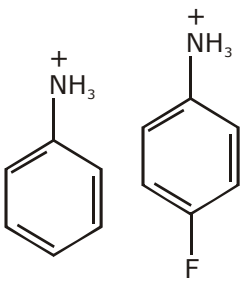
(ii) Benzoic acid to meta - fluorobenzoic acid in not more than three steps.

Sol.

25. There is a solution of p-hydroxybenzoic acid and p-amino benzoic acid. Discuss one method by which we can separate them and also write down the confirmatory test of the functional group present. **[JEE 2003]**

Sol.

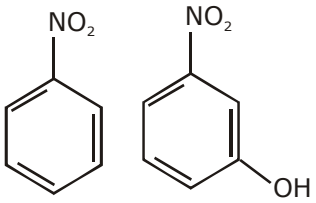
26. Which of the following is more acidic and why ? **[JEE 2004]**



(I) (II)

Sol.

27. Convert



in not more than four steps. Also mention the reaction conditions and temperature. **[JEE 2004]**

Sol.

Answers

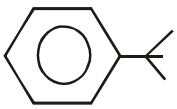
Answer Ex–I OBJECTIVE PROBLEMS (JEE MAIN)

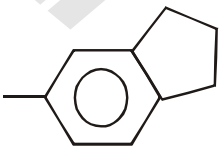
1. A	2. D	3. B	4. B	5.D	6. D	7. D
8. B	9. B	10. A	11. A	12. C	13. B	14. B
15. B	16. C	17. B	18. A	19. D	20. D	21. B
22. C	23. B	24. B	25. A	26. D	27. C	28. D
29. B	30. B	31. D	32. C	33. A	34. B	35. D
36. A	37. D	38. A	39. B	40. B	41. A	42. B
43. B	44. B	45. D	46. B	47. C	48. C	49. D
50. C	51. D	52. A	53. D	54. C	55. D	56. D
57. A	58. B	59. A	60. A	61. C	62. B	67. C
64. C	65. A	66. C	67. C	68. A	69. D	70. C
71. B	72. D	73. C	74. C	75. A	76. A	77. A
78. C	79. C	80. A	81. D	82. D	83. D	84. B
85. B	86. B	87. A	88. C	89. B	90. A	

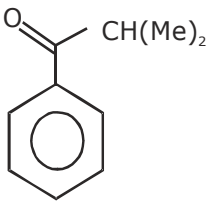
Answer Ex–II OBJECTIVE PROBLEMS (JEE ADVANCED)

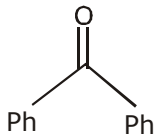
1. B	2. B	3. D	4. A	5. D	6. A	7. B
8. D	9. A	10. B	11. B	12. A,C	13. A,B	14. A,B,C,D
15. A,B,C,D	16. A,B	17. A,B,C	18. A,B,C	19. A,B,D	20. A,B	21. A
22. C,D	23. B	24. C	25. C	26. B,C,D	27. B	28. B,D
29. C,D	30. B, C	31. B	32. A	33. C		

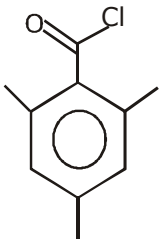
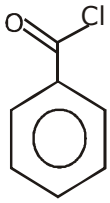
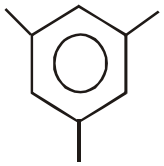
Answer Ex–III SUBJECTIVE PROBLEMS (JEE ADVANCED)

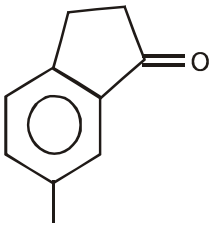
1. 

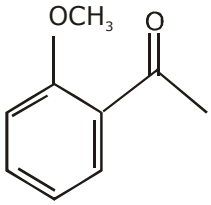
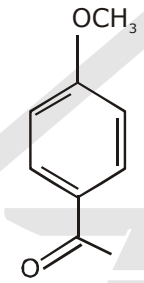
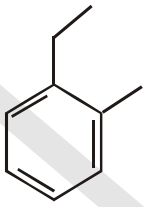
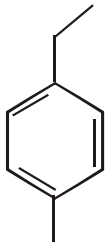
2. 

3. (A) 

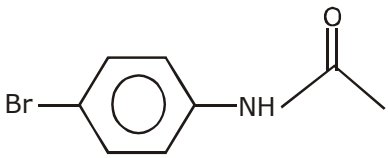
(B) 

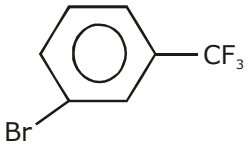
4. (i)  +  $\xrightarrow{AlCl_3}$ (ii)  +  $\xrightarrow{AlCl_3}$

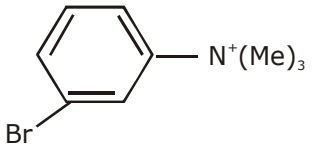
5. 

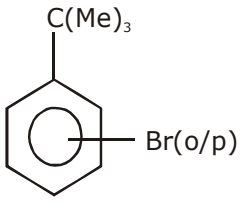
6. (1)  +  (b)  

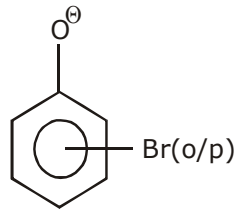
7. o , p - directing

8. (A) (o/p) 

(B) (meta) 

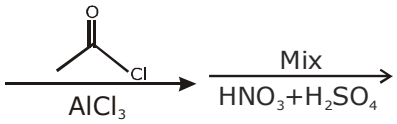
(C)  (meta)

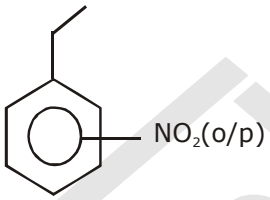
(D) 

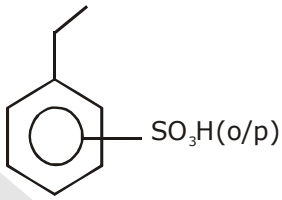
(E) 

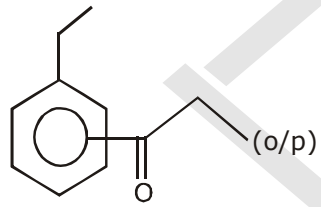
9. Due to effecive delocalization of 2p-2p in comparison to 2p-3p, that's why anisole is more reactive towards nitration.

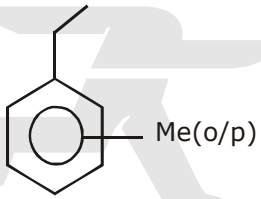
10. – NMe_2 group is + M effecting group

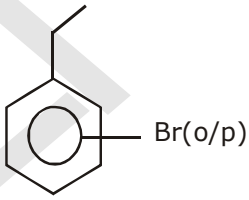
11. Benzene 

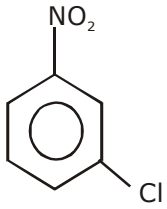
12. (a) No reaction. (b) 

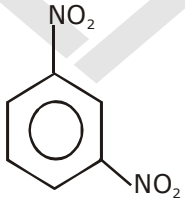
(c) 

(d) 

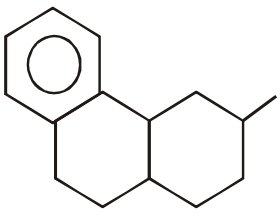
(e) 

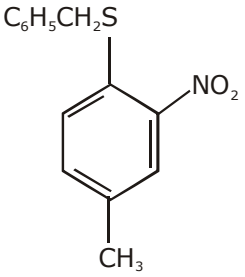
(f) 

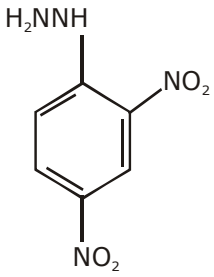
13. (1) 

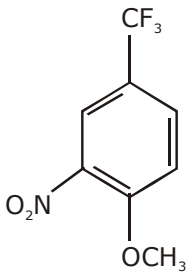
(B) 

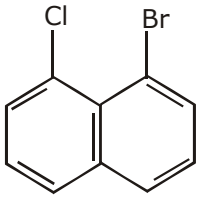
(C) No reaction

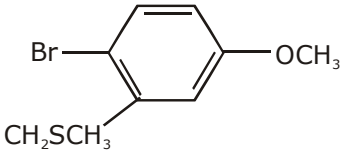
14. 

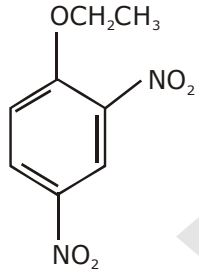
15. (i) 

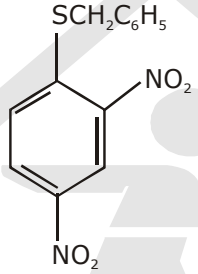
(ii) 

(iii) 

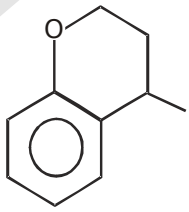
(iv) 

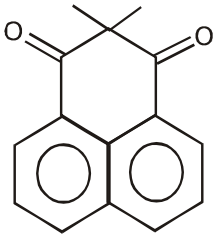
(v) 

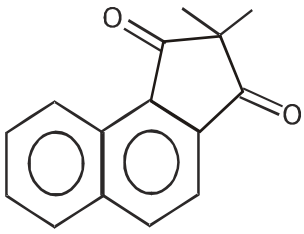
(vi) 

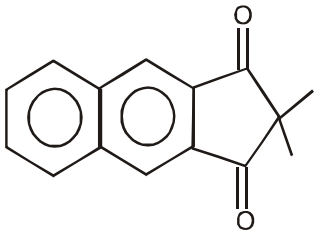
(vii) 

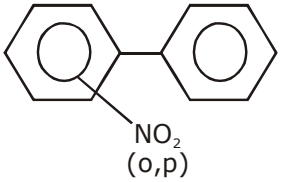
16. (a) 

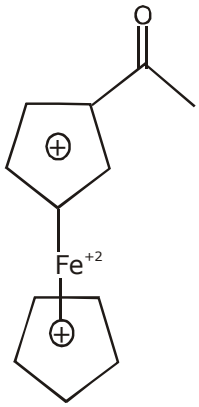
(b) 

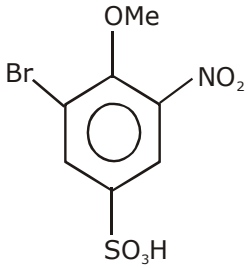
(c) 

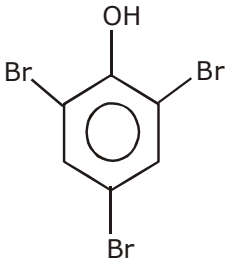


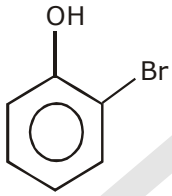


(d) 

(e) 

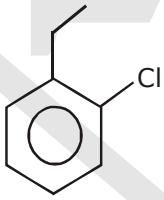
(f) 

17. 



and


18. 

and


(1) (B)

19. A $\rightarrow$P , R ; B $\rightarrow$ P, R ; C $\rightarrow$ P , R ; D $\rightarrow$ P , S
20. A $\rightarrow$ Q , S ; B $\rightarrow$ P , R ; C $\rightarrow$ R ; D $\rightarrow$ P
21. A $\rightarrow$P ,R ; B $\rightarrow$ P , R ; C $\rightarrow$ P , R ; D $\rightarrow$ P , R
22. A $\rightarrow$P ,R ,S ; B $\rightarrow$ P , R ; C $\rightarrow$ Q ,S D $\rightarrow$ Q, R, S

23. A $\rightarrow$P ; B $\rightarrow$ Q ; C $\rightarrow$ R ; D $\rightarrow$ S

24. A $\rightarrow$ Q ; B $\rightarrow$ P $\rightarrow$; C $\rightarrow$ Q ; D $\rightarrow$ Q

25. A → P,Q ; B → Q , S ; C → P ; D → R

26. A → P ; B → P, ; C → Q, ; D → R , S

27. A →P, R B → P, R, S ; C → Q, R ; D → P , R

28. A → P , S ; B → P, R, ; C → P ,Q ; → D,→ T

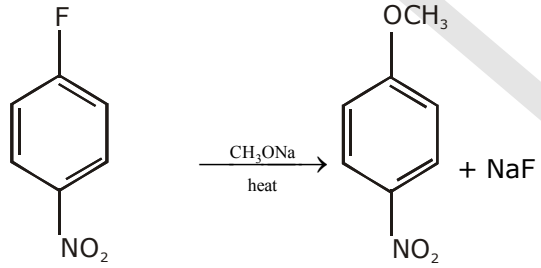
29. C 30. D 31. C

Exercise-IV (level-1)

1.	**A**	**2.**	**A**	**3.**	**C**	**4.**	**A**	**5.**	**D**
6.	**A**	**7.**	**A**	**8.**	**D**	**9.**	**A**	**10.**	**B**
11.	**B**	**12.**	**C**	**13.**	**D**	**14.**	**C**	**15.**	**D**
16.	**A**								

Exercise-IV (level-2)

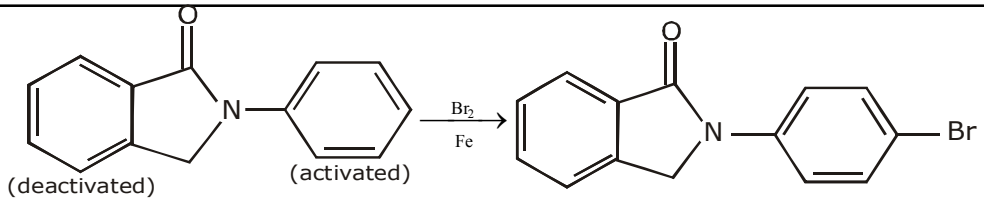
1 A	2. D	3. C	4. B	5. D		
6. C	7. C	8. C	9. C	10. B	11. B	12. D
13. C	14.D	15. C	16. C	17. A,C		

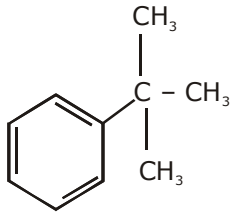
18. 

+ NaF

Nucleophilic aromatic substitution occur which is assisted by electron withdrawing – NO_2 group from para position.

19. $C_6H_5NH_2 \xrightarrow[HCl/°C]{NaNO_2} C_6H_5N^+{}_2Cl^- \xrightarrow{CuCN} C_6H_5CN \xrightarrow[\text{or } H_2.Ni]{LIAlH_4} C_6H_5 - CH_2NH_2$

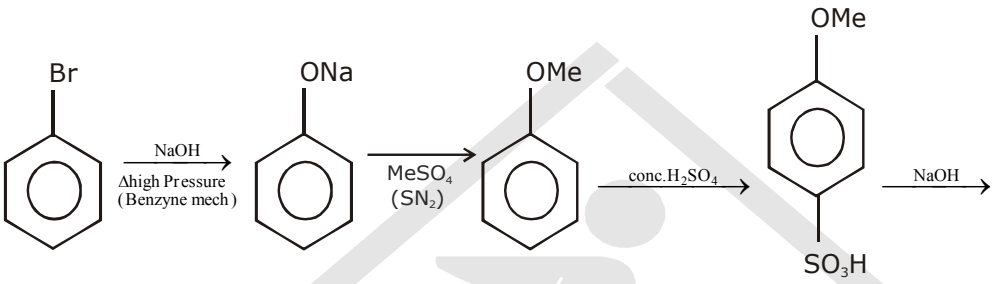
20. 

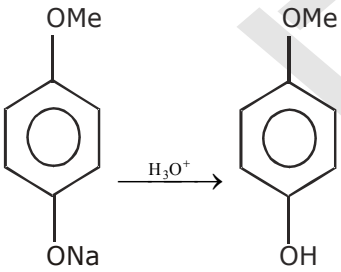
21. (i) 

+ $KMnO_4$ ⟶ No oxidation takes place

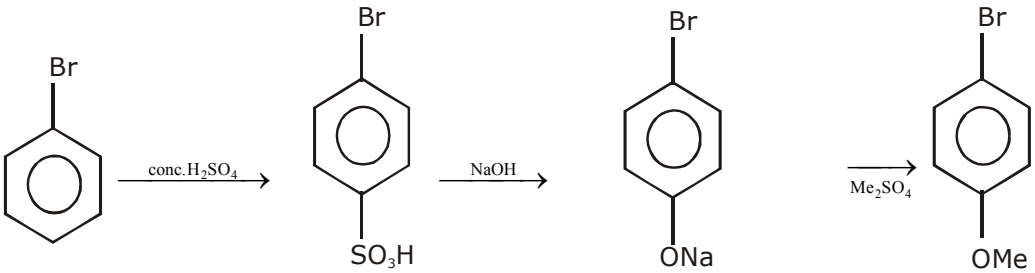
tert butyl benzene
(no. a – H)

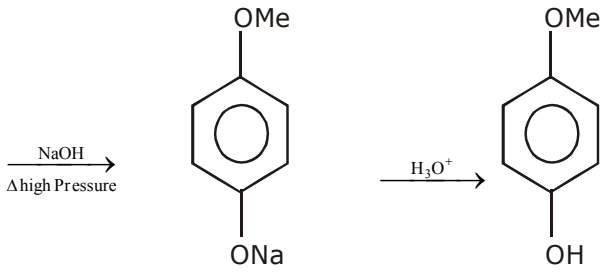
(ii) Pi - electrons of double bonds are involved in aromatic delocalisation (aromaticity). However electrophilic addition do not ocour as it would distroy aromatic stability however electrophilic substitution do not destroy asomaticity

22. 

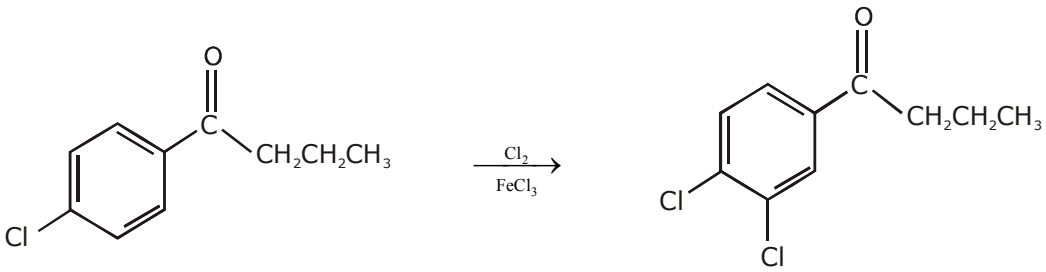


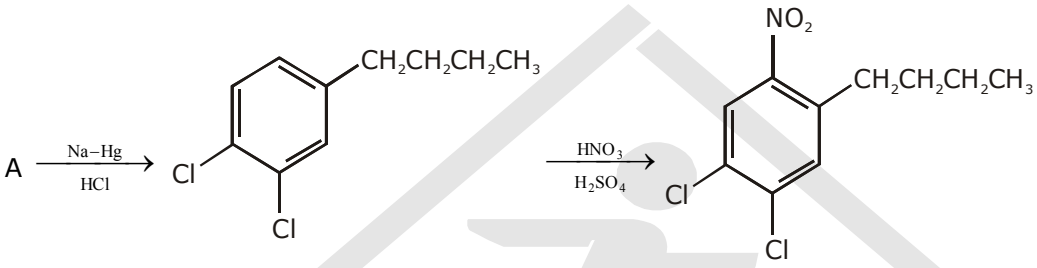
Alternative rout

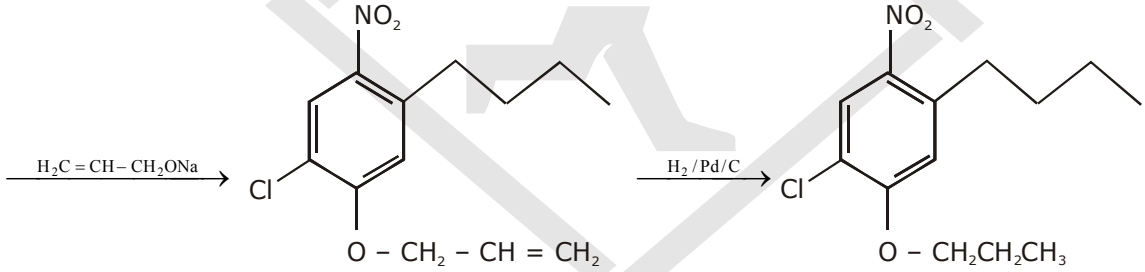




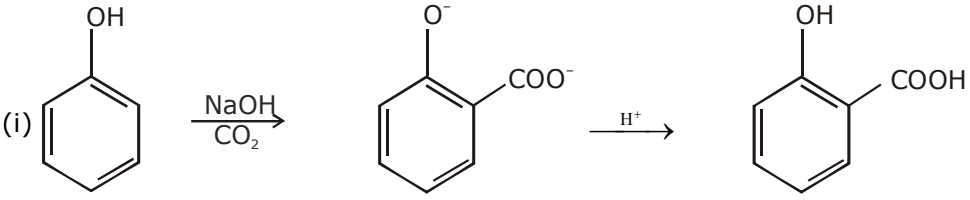
23.



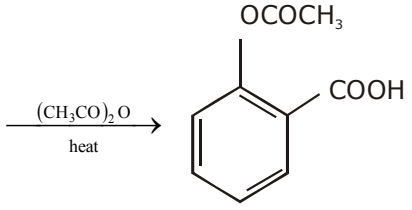




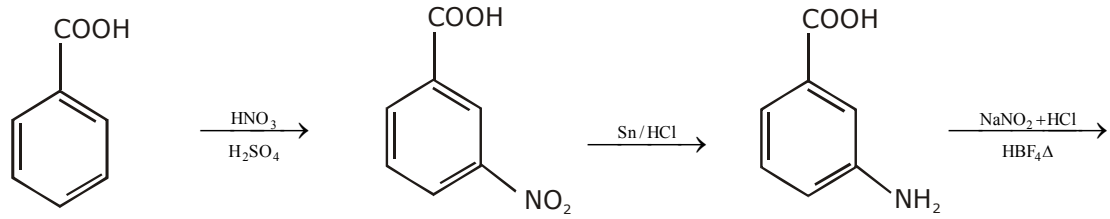
24. (i)

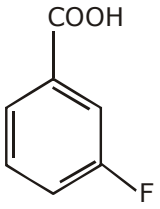


Kolbe's reaction

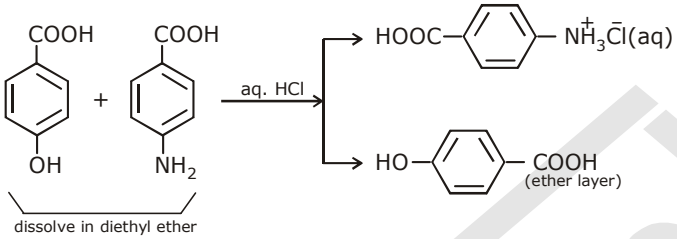


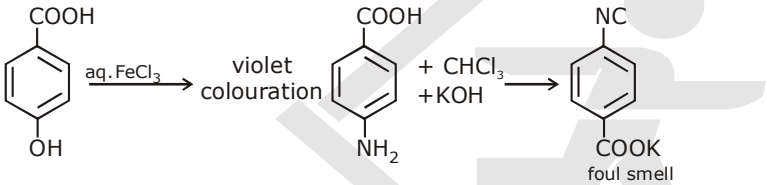
aspirin

(ii) 

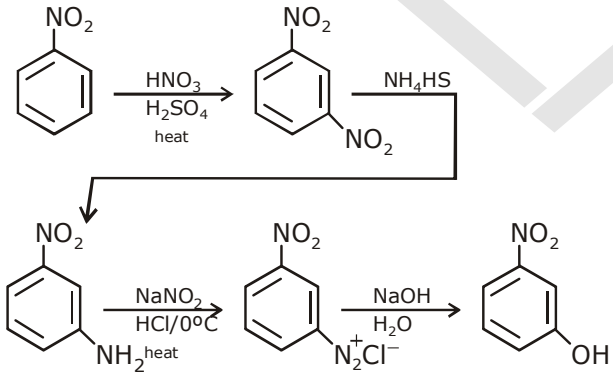


meta - fluorobenzoic acid

25. 

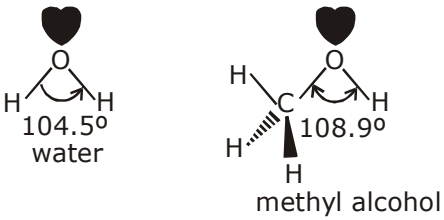


26. II is more acidic due to – I effect of F.

27. 

ALCOHOL

Introduction

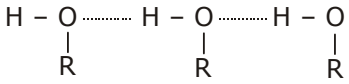


Physical Properties

(1) Boiling point :

(a) Alcohols show increase in boiling point with increase in molecular weight amongst homologues.

(b) Alcohols have higher boiling point than hydrocarbons of the same molecular weight. The reason for higher boiling point is the intermolecular H-bonding present in alcohols.



Intermolecular H bonds in alcohol

(2) Solubility in water :

As molecular weight increases solubility in water decreases. The lower alcohols are miscible with water. This is due to intermolecular hydrogen bonding between alcohol and water molecules.

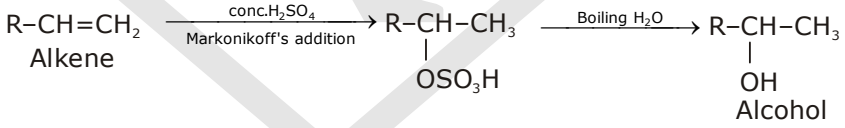
Intermolecular H bond between water & alcohol molecules

Preparation of alcohols

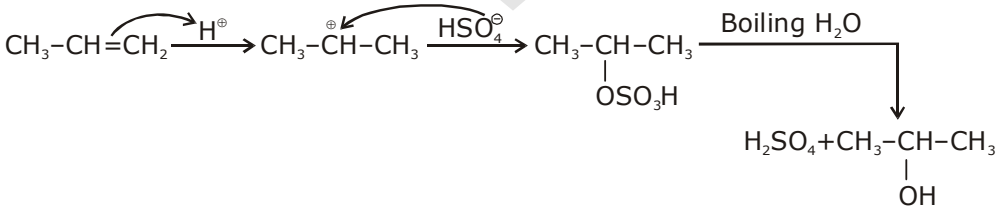
(1) From alkenes

(a) By acid catalyzed hydration of alkenes : Formation of carbocation intermediate (Markovnikov addition, rearrangement possible)

General reacion



e.g.



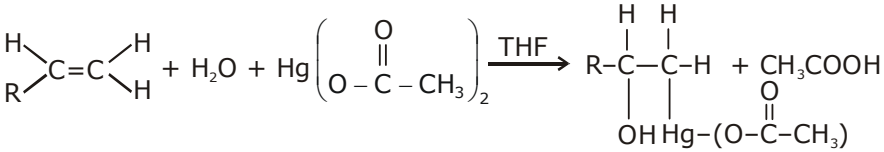
(b) By Oxymercuration - demercuration process :

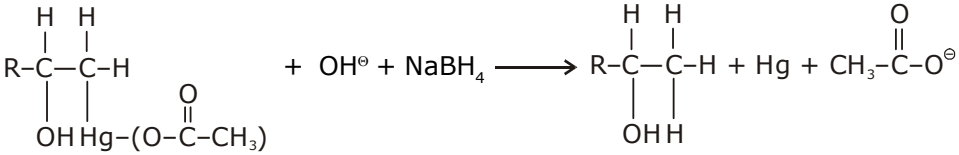
(1) Oxymercuration involves an electrophilic attack on the double bond by the positively charged mercury species. The product is a mercurinium ion, an organometallic cation containing a three-membered ring.

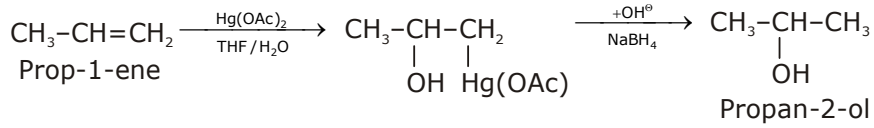
(2) In the second step, water from the solvent attacks the mercurinium ion to give (after deprotonation) an organomercurial alcohol.

(3) The third step is demercuration to remove the Hg. Sodium borohydride ($NaBH_4$, a reducing agent) re-places the mercuric acetate fragment with hydrogen.

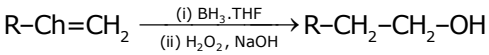
General reaction

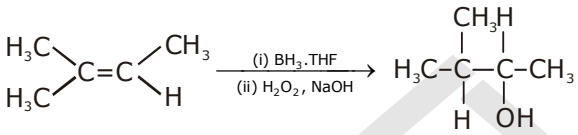




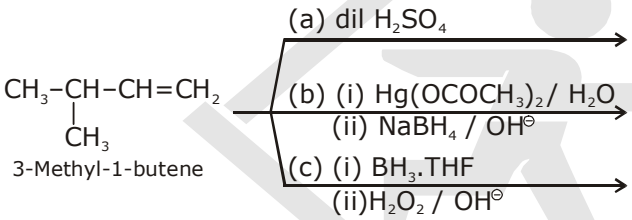
e.g. 

(c) By Hydroboration - oxidation process : (Forms anti-markovnikov alcohol, no rearrangement)

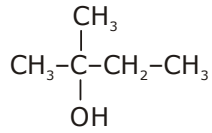
General reaction 

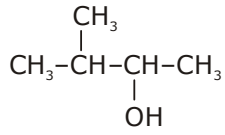
e.g. 

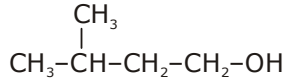
Ex. Give the major product of the following reaction



Ans. Major product is

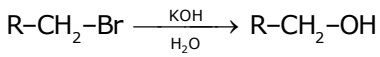
(a)  because 3° carbocation is more stable.

(b) 

(c) 

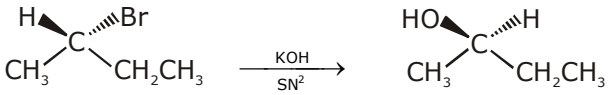
(2) From alkyl halides : By nucleophilic substitution reactions

(a) By SN^2 mechanism (second-order substitution) : It is given by primary (and some secondary) halides

General reaction : 

e.g. $(CH_3)_2CHCH_2CH_2–Br \xrightarrow[H_2O]{KOH} (CH_3)_2CHCH_2CH_2–OH$

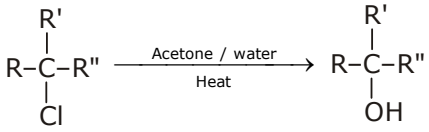
e.g.



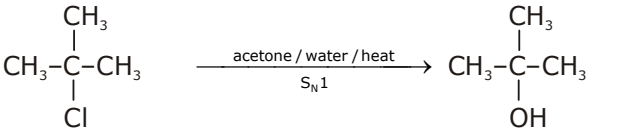
(S)-2-Bromobutane (R)-2-utanol
100% inverted configuration

(b) By SN^1 mechanism : It is given by tertiary and some secondary halides

General reaction :



e.g.



Tert-butyl chloride Tert-butyl alcohol

(3) From Grignard reagents

(a) From air

A Grignard reagent may be used to synthesize an alcohol by treating it with dry oxygen and decomposing the product with acid :

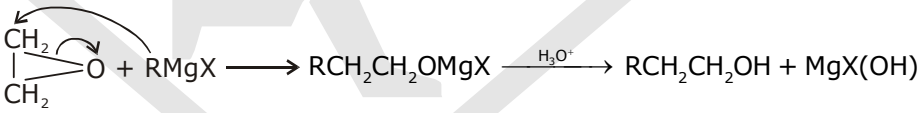
General reaction $RMgX \xrightarrow{O_2} RO_2MgX \xrightarrow{RMgX} 2ROMgX \xrightarrow{H_3O^+} 2ROH$

e.g. $C_2H_5MgBr \xrightarrow{O_2} C_2H_5O_2MgX \xrightarrow{C_2H_5MgX} 2C_2H_5OMgX \xrightarrow{H_3O^+} 2C_2H_5OH + MgBr(OH)$

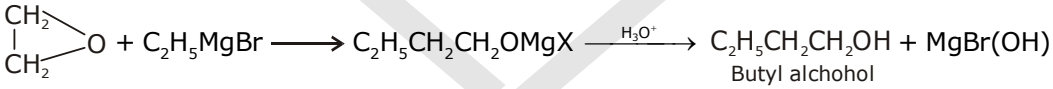
(b) From ethylene oxide

Addition of Grignard reagent to ethylene oxide gives a primary alcohol (with two carbon atoms added)

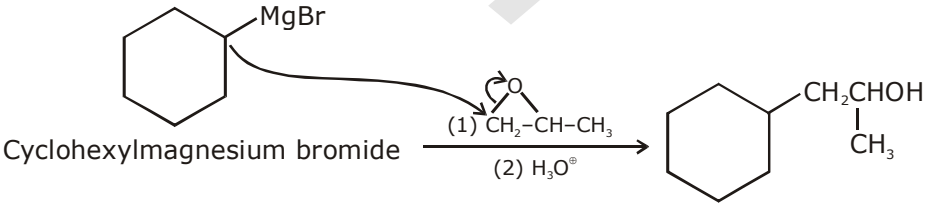
General reaction



e.g.



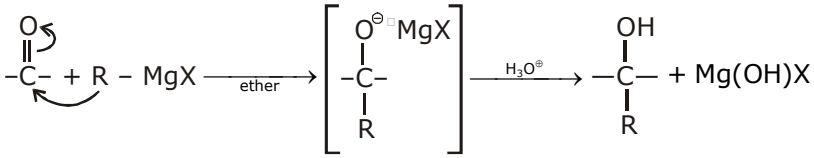
Butyl alchohol



Cyclohexylmagnesium bromide

(c) From carbonyl compounds : Nucleophilic addition to the carbonyl groups by Grignard reagent

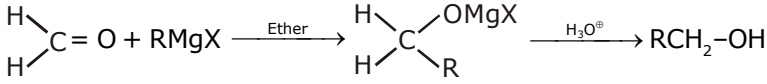
General reaction



adduct

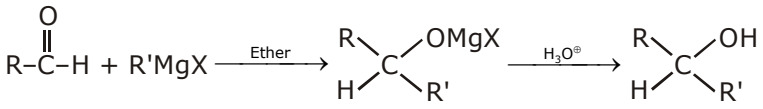
(i) Addition of formaldehyde gives a primary alcohol

General reaction



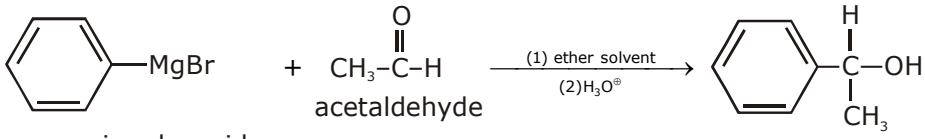
(ii) Addition to an aldehyde (other than formaldehyde) gives a secondary alcohol

General reaction



(sec-alcohol)

e.g.



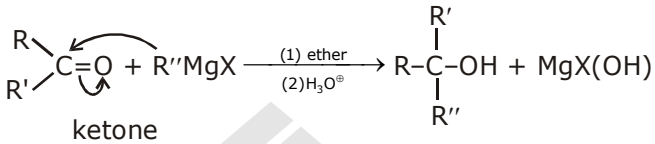
Phenylmagnesium bromide

acetaldehyde

1-phenylethanol

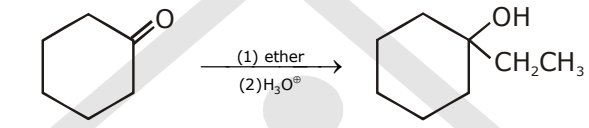
(iii) Addition to a ketone gives a tertiary alcohol

General reaction



ketone

e.g. CH_3CH_2MgCl +



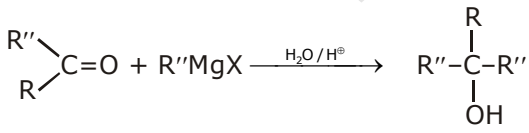
Cyclohexanone

1-Ethylcyclohexanol

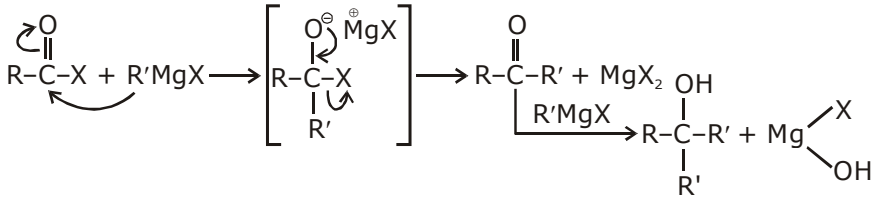
(iv) Addition to an acid halide or an ester gives a tertiary alcohol

Esters on treatment with Grignard ragent first form ketones which then react with second molecule of Grignard reagent and form tertiary alcohol.

General reaction



tertiaryalcohol



(4) By reduction of carbonyl compounds

(a) Catalytic hydrogenation of aldehydes and ketones

General reaction

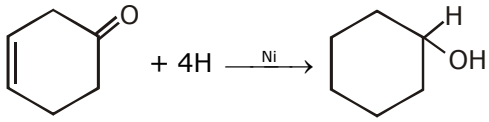
$$\underset{\text{Aldehyde}}{R-CHO} \xrightarrow{H_2/Ni} \underset{1^\circ\text{Alcohol}}{R-CH_2OH}$$

$$\underset{\text{Ketone}}{R_2C=O} \xrightarrow{H_2/Ni} \underset{2^\circ\text{Alcohol}}{R_2CH-OH}$$

e.g.

$$CH_3CHO + 2H \xrightarrow{H_2/Ni} CH_3CH_2OH$$

$$\underset{\text{(Acrolein)}}{CH_2=CHCHO} + 4H \xrightarrow[\text{Catalyst}]{Ni} CH_3CH_2CH_2OH$$



(b) Lithium aluminium hydride reduction of aldehydes and ketones

General reaction

(i) $\underset{\text{Aldehyde}}{R-CHO} \xrightarrow{LiAlH_4} \underset{1^\circ\text{Alcohol}}{R-CH_2OH}$

(ii) $\underset{\text{Ketone}}{R_2C=O} \xrightarrow{LiAlH_4} \underset{2^\circ\text{Alcohol}}{R_2CH-OH}$

(iii) $RCOOH + 4H \xrightarrow{LiAlH_4} RCH_2OH + H_2O$

(iv) $R-\underset{\underset{O}{\|}}{C}-Cl + 4H \xrightarrow{LiAlH_4} RCH_2OH + HCl$

(v) $R-\underset{\underset{O}{\|}}{C}-O-R' \xrightarrow{LiAlH_4} R-CH_2OH + R'OH$

e.g.

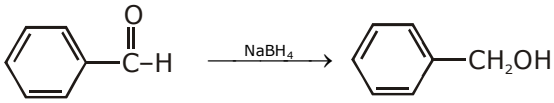
$$CH_3-\overset{\overset{O}{\|}}{C}-O-H \xrightarrow{LiAlH_4} CH_3CH_2OH$$

$$C_2H_5-\overset{\overset{O}{\|}}{C}-Cl + 4H \longrightarrow C_2H_5CH_2OH + HCl$$

(c) By $NaBH_4$ (sodium borohydride) : It is insoluble in ether and is used in aqueous ethanolic solution to reduce carbonyl compounds. It does not reduce esters and acids.

$$R-\overset{\overset{O}{\|}}{C}-H \xrightarrow{NaBH_4} R-CH_2-OH$$

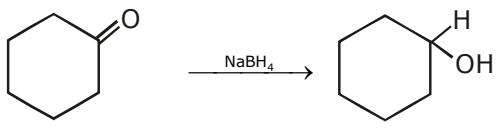
e.g.



benzaidehyde benzyl alcohol

$$CH_3CH=CHCHO + 4H \xrightarrow{NaBH_4} CH_3CH=CHCH_2OH$$

(ii) Reduction of a ketone gives a secondary alcohol



Cyclohexanone Cyclohexanol

(d) Bouveault-Blanc reduction : The reduction of aldehydes, ketones or esters by means of excess of sodium and ethanol or n-butanol as the reducing agent.

General reaction

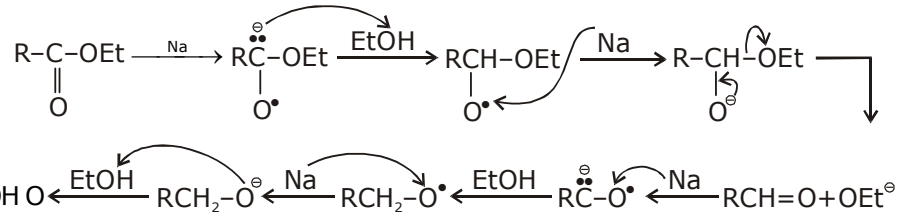
(i) Aldehyde $RCHO \xrightarrow[EtOH]{Na} RCH_2OH$

(ii) Esters $R'CO_2R'' \xrightarrow[EtOH]{Na} R'CH_2OH + R''OH$

(iii) Ketones $R_2CO \xrightarrow[EtOH]{Na} R_2CHOH$

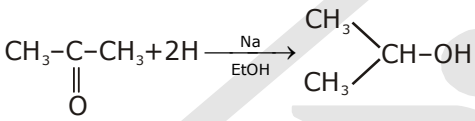
The Bouveault-Blanc reduction is believed to occur in steps involving transfer of one electron at a time.

Mechanism

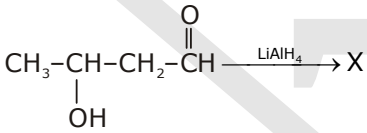


e.g. $CH_3CHO + 2H \xrightarrow[EtOH]{Na} CH_3CH_2OH$

$CH_3COOC_2H_5 + 4H \xrightarrow[EtOH]{Na} 2CH_3CH_2OH$

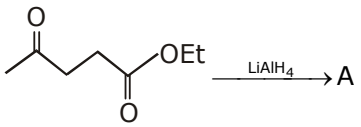


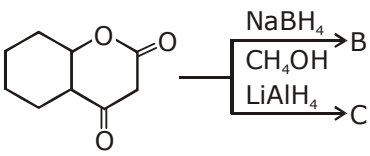
Ex. Identify (X) in the following reaction

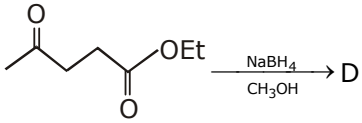


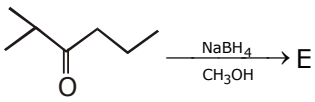
Ans. $X = CH_3-CH(OH)-CH_2-CH_2-OH$

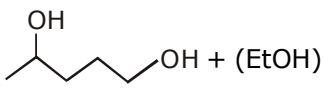
Ex. What are the product A, B, C, D and E in the following reactions?

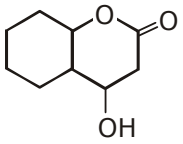


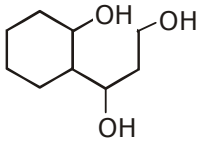


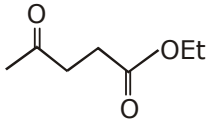


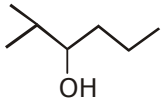


Ans. A : 

B :  Ester part is not affected by $NaBH_4$

C :  Ester part and keto parts are affected by $LiAlH_4$

D : 

E : 

(5) By reaction of nitrous acid on aliphatic primary amines

General reaction $R-NH_2+HONO \xrightarrow{NaNO_2/HCl} R-OH + N_2 + H_2O$

Mech.

$$R-NH_2 \xrightarrow{HNO_2} (RN_2^{\oplus}) \xrightarrow{H_2O} ROH + N_2 + H^{\oplus}$$

e.g. (i) $C_2H_5NH_2 + HNO_2 \longrightarrow C_2H_5OH + N_2 + H_2O$

(ii) $CH_3-CH_2-\underset{\displaystyle NH_2}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}-CH_3 + HONO \xrightarrow{NaNO_2/HCl} CH_3-CH_2-\underset{\displaystyle OH}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}-CH_3 + N_2 + H_2O$

Mech.

$$CH_3-CH_2-\underset{\displaystyle NH_2}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}-CH_3 \xrightarrow{HONO} CH_3-CH_2-\underset{\displaystyle OH}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}-CH_3 \xleftarrow{H_2O} CH_3-CH_2-\overset{\displaystyle CH_3}{\overset{|}{\underset{\oplus}{C}}}-CH_3$$

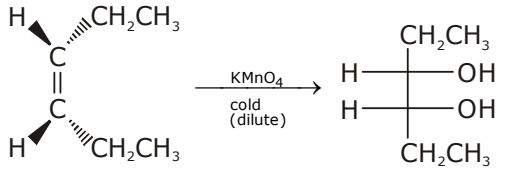
(6) Hydroxylation : Forms vicinal diols (glycols)

Converting an alkene to a glycol requires adding a hydroxy group to each end of the double bond. This addition is called hydroxylation of the double bond.

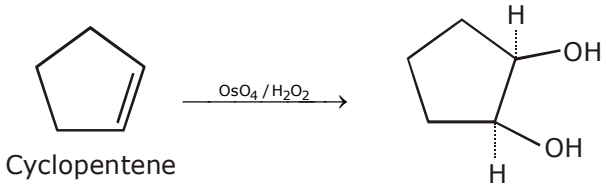
(a) Syn hydroxylation, using $KMnO_4$ / NaOH or using OsO_4/H_2O_2

General reaction :

$$>C=C< \xrightarrow[\text{or } KMnO_4, OH^{\ominus}\ (\text{cold, dilute})]{OsO_4, H_2O_2} -\underset{\displaystyle HO}{\overset{|}{C}}-\underset{\displaystyle OH}{\overset{|}{C}}-$$

e.g. 

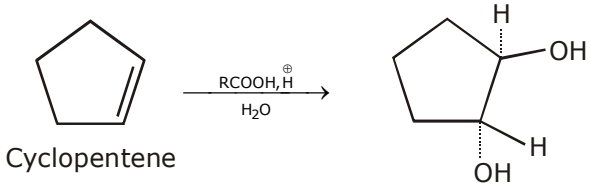
cis-3-hexene



Cyclopentene

cis-Cyclopentane-1, 2-diol

(b) Anti hydroxylation, using per acids



Cyclopentene

trans-Cyclopentane-1, 2-diol

Chemical reactions of alcohols

1. Reaction with hydrogen halides

General reaction :

$R - OH + HX \longrightarrow R - X + H_2O$ (R may rearrange)

Reactivity of HX : HI > HBr > HCl

Reactivity of ROH: allyl, benzyl > 3° > 2° > 1°

Mechanism $R - OH \xrightarrow{H^{\oplus}} R-\overset{\oplus}{O}H_2 \longrightarrow \overset{\oplus}{R} \xrightarrow{X^{\ominus}} R-X$

e.g. $CH_3\underset{\underset{OH}{|}}{CH}CH_3 \xrightarrow[\text{or } NaBr, H_2SO_4]{\text{cons. HBr}} CH_3\underset{\underset{Br}{|}}{CH}CH_3$ (reflux)

Isopropyl alcohol — Isopropyl bromide

e.g. $CH_3CH_2CH_2CH_2CH_2OH \xrightarrow[\text{heat}]{\text{HCl, (anhydrous) } ZnCl_2,\ \text{Lucas reagent}} CH_3CH_2CH_2CH_2CH_2Cl$

n-Pentyl alcohol — n-Pentyl chloride

e.g. $CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \xrightarrow[\text{room temp.}]{\text{conc. HCl}} CH_3-\underset{\underset{Cl}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$

tert- Butyl alcohol — tert-Butyl chloride

2. Reaction with Phosphorus trihalides

(1) Several phosphorus halides are useful for converting alcohols to alkyl halides. PBr_3, PCl_3, & PCl_5 work well and are commercially available.

(2) Phosphorus halides produce good yields of most primary and secondary alkyl halides, but none works well with ter. alcohols. The two phosphorus halides used most often are PBr_3 and the P_4 / I_2 combination.

General reaction :

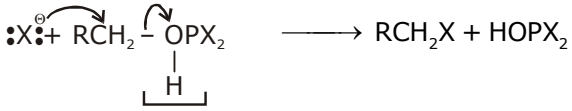
$3R - OH + PX_3 \xrightarrow{(PX_3 = PCl_3, PBr_3, PI_3)} 3R - X + H_3PO_3$

Mechanism

The mechanism for the reaction involves attach of the alcohol group on the phosphorus atom, displacing a bromide ion and forming a protonated alkyl dibromophosphite (see following reaction).

Protonated
alkyl dibromophosphite

In second step a bromide ion acts as nucleophile to displace $HOPBr_2$, a good leaving group due to the electronegative atoms bonded to the phosphorus.



A good leaving group

e.g. $CH_3CH_2CHCH_2OH$ (CH_3 on the second carbon) $\xrightarrow{PBr_3}$ $CH_3CH_2CHCH_2Br$

2–Methyl–1–butanol → 2–Methyl–1–bromobutane

$CH_3CH_2OH \xrightarrow{P+I_2} CH_3CH_2I$

Ethyl alcohol → Ethyl iodide

3. Reaction with thionyl chloride

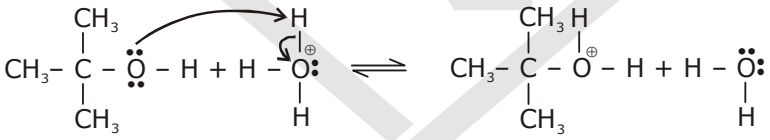
$$R{-}OH + Cl{-}\overset{\overset{O}{\|}}{S}{-}Cl \xrightarrow{Heat} R{-}Cl + SO_2 + HCl$$

4. Dehydration of alcohols

(Rearrangement may occur)

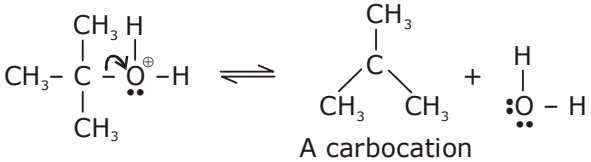
Mechanism

Step 1 :



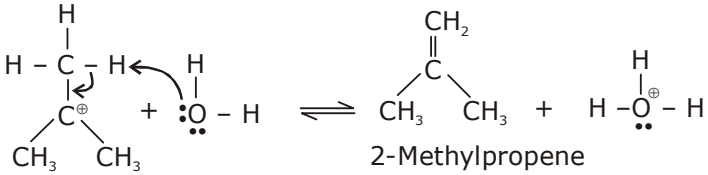
Protonated alcohol
or alkyloxonium ion

Step 2 :



A carbocation

Step 3 :



2-Methylpropene

Reactivity of ROH : $3^o > 2^o > 1^o$

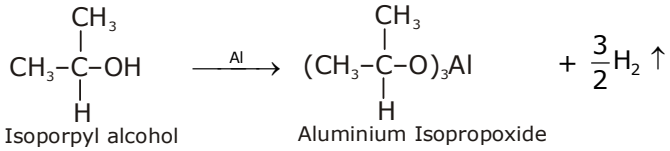
5. Reaction with metals

$RO-H+M \longrightarrow RO^{\ominus}M^{\oplus} + \frac{1}{2}H_2$ M=Na, K, Mg, Al, etc

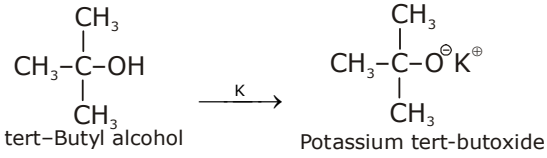
Reactivity order of ROH: $CH_3OH > 1^{\circ} > 2^{\circ} > 3^{\circ}$

e.g. $CH_3CH_2OH \xrightarrow{Na} CH_3CH_2O^{\ominus}M^{\oplus} + \frac{1}{2}H_2$

Ethyl alcohol — Sodium ethoxide



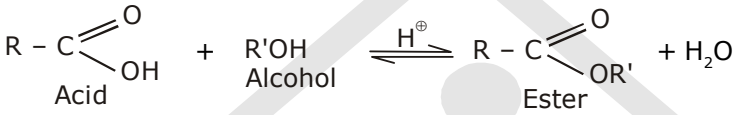
Isoporpyl alcohol — Aluminium Isopropoxide



tert–Butyl alcohol — Potassium tert-butoxide

6. Ester formation

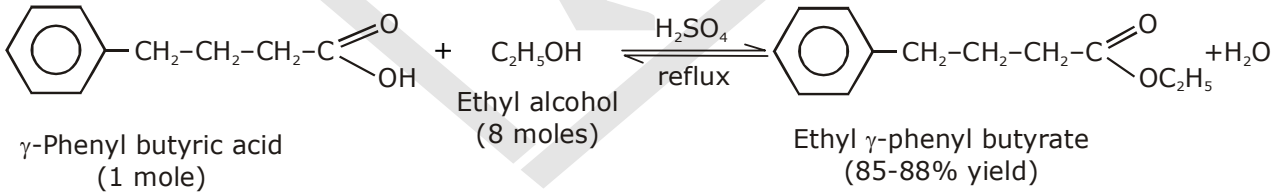
General reaction



Acid — Alcohol — Ester

e.g. $CH_3CH_2O-H + CH_3C(=O)OH \xrightarrow{H^{\oplus}} CH_3C(=O)OC_2H_5 + H_2O$

Acetic acid — Ethyl acetate



γ-Phenyl butyric acid (1 mole) — Ethyl alcohol (8 moles) — Ethyl γ-phenyl butyrate (85-88% yield)

7. Oxidation reactions

(a) oxidation of primary alcohols

Oxidation of a primary alcohol initially forms an aldehyde. obtaining the aldehyde is often difficult, since most oxidizing agents are strong enough to oxidize the adehydes formed. CrO_3 acid generally oxidizes a primary alcohol all the way upto the carboxylic acid

(b) oxidation of secondary aldohols

Sec. alcohols are easily oxidized to give excellent yields of ketones. The chromic acid reagent is often best for laboratory oxidations of secondary alcohols. The active species in the mixture is probably chromic acid,

H_2CrO_4, or the acid chromate ion, $HCrO_4^{\ominus}$

(c) Resistance of tertiary alcohols to oxidation

Oxidation of ter-alcohol is not an important reaction is organic chemistry. Ter-alcohols have hydrogen atoms on the carbinol carbon atom, so oxidation must take place by breaking C–C bonds. These oxidations require severe conditions and result in mixtures of products.

Primary $R-CH_2OH \xrightarrow{C_2H_5NH^{\oplus}CrO_3Cl^{\ominus}} R-\underset{H}{\overset{|}{C}}=O$ An aldehyde

$R-CH_2OH \xrightarrow{KMnO_4} R-COOH$ A carboxylic acid

Secondary $R-\underset{R}{\overset{|}{C}}HOH \xrightarrow{K_2Cr_2O_7 \text{ or } CrO_3/H^{\oplus}} R-\underset{R}{\overset{|}{C}}=O$ A ketone

Tertiary $R-\underset{R}{\overset{R}{\overset{|}{\underset{|}{C}}}}-OH \xrightarrow{KMnO_4}$ no reaction

e.g.

$CH_3CH_2CH_2OH \xrightarrow{C_5H_5NH^{\oplus}CrO_3Cl^{\ominus}} CH_3CH_2\underset{H}{\overset{|}{C}}=O$

n-Propyl alcohol (1°) — Propionaldehyde

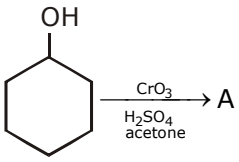
$CH_3CH_2\underset{CH_3}{\overset{|}{C}}HCH_2OH \xrightarrow{KMnO_4} CH_3CH_2\underset{CH_3}{\overset{|}{C}}HCOOH$

2-Methyl-1-butanol (1°) — 2-Methylbutanoic acid

$CH_3CH_2\underset{OH}{\overset{|}{C}}HCH_2CH_3 \xrightarrow{CrO_3/H^{\oplus}} CH_3CH_2\overset{O}{\overset{\|}{C}}CH_2CH_3$

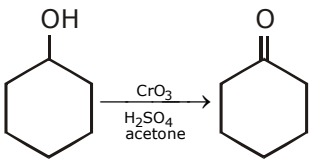
3-Pentanol (2°) — 3-Pentanone

Ex.



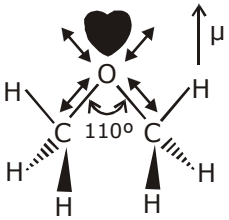
Identify A

Ans.

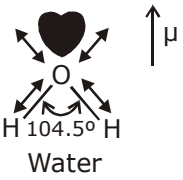


ETHER

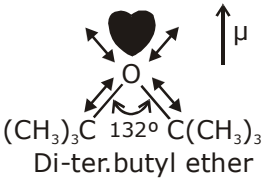
Structure of ether



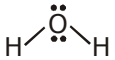
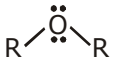
dimethyl ether



Water



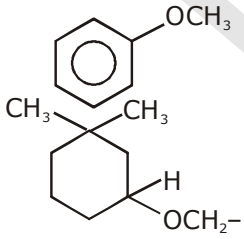
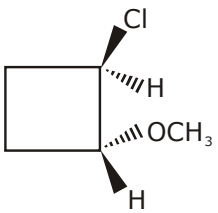
Di-ter.butyl ether

Compound	Hybridization	Bond angle
 water	sp^3	104.5°
 Alcohol	sp^3	108.5°
 Ether	sp^3	111.7°

Classificaion of Acyclic ethers

S.No.	Type	Example	Name
1	Simple ether	$CH_3–O–CH_3$	Methoxy methane
		$CH_3–CH_2–O–CH_2–CH_3$	Ethoxy ethane
2	Mixed ether	$CH_3–O–CH_2–CH_3$	Methoxy ethane

IUPAC Nomenclature of ether "Alkoxy Alkane"

S.N.	Compound	IUPAC Name
1.	$CH_3–\underset{\displaystyle CH_3}{\underset{\vert}{CH}}–O–CH_3$	2-Methoxy propane
2.	$Cl–CH_2–O–CH_3$	Chloromethoxy methane
3.		Methoxy benzene (Anisole)
4.		3-Ethoxy-1, 1-dimethyl cyclohexane
5.		trans-1-Chloro-2-methoxy cyclobutane
6.	$\underset{\displaystyle CH_2–O–CH_2–CH_3}{\underset{\vert}{CH_2–OH}}$	2-Ethoxy ethan-1-ol

Method of Preparation of Ether

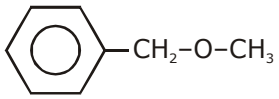
(1) Williamson synthesis

General reaction

$$RX + R'O^{\ominus}Na^{\oplus} \longrightarrow R - OR'$$

e.g. (i) $n\text{-PrOH} \xrightarrow{n\text{-PrBr}} CH_3CH_2CH_2O{-}CH_2CH_2CH_3$

Di-n-propyl ether

(ii) $MeOH \xrightarrow{Na} MeO^{\ominus} \xrightarrow{PhCH_2Br}$  $CH_2{-}O{-}CH_3$

Benzylmethyl ether

(iii) $t\text{-BuOH} \xrightarrow{Na} t\text{-BuO}^{\ominus} \xrightarrow{EtBr}$ t-Butyl ethyl ether

(This reaction produces a poor yield of ether because of the bulkiness of $t\text{-BuO}^-$)

2. Williamson's Continuous Etherification process or by Dehydration of Alcohols

(i) $ROH + \overset{\oplus}{H} \longrightarrow RO\overset{\oplus}{H}_2$

$$R\ddot{O}H + R - \overset{\oplus}{O}H_2 \xrightarrow{S_N^2} R_2\overset{\oplus}{O}H + H_2O \longrightarrow ROR + H_3O^{\oplus}$$

(ii) $ROH + \overset{\oplus}{H} \longrightarrow RO\overset{\oplus}{H}_2 \longrightarrow \overset{\oplus}{R}$ .... S_N^1

$$R\ddot{O}H + R \longrightarrow \underset{H}{\overset{\oplus}{R}}OR \longrightarrow ROR$$

e.g. CH_3CH_2OH

$\xrightarrow[180^\circ C]{H_2SO_4}$ $CH_2{=}CH_2$ Ethene

$\xrightarrow[140^\circ C]{H_2SO_4}$ $CH_3CH_2OCH_2CH_3$ Diethyl ethene

Mechanism

Step-1: $CH_3CH_2{-}\ddot{O}{-}H + H{-}OSO_3H \rightleftharpoons CH_3CH_2{-}\overset{\oplus}{\underset{H}{O}}{-}H + {}^-OSO_3H$

This is an acid-base reaction in which the alcohol accepts a proton from the sulfuric acid

Step-2 : $CH_3CH_2{-}\ddot{O}{-}H + CH_3CH_2{-}\overset{\oplus}{\underset{H}{O}}{-}H \rightleftharpoons$

Another molecule of the alcohol acts as a nucleophile and attacks the protonated alcohol in an S_N^2 reaction.

Step-3 : $CH_3CH_2{-}\overset{\oplus}{\underset{H}{O}}{-}CH_2CH_3 + \ddot{O}{-}H \rightleftharpoons CH_3CH_2{-}\ddot{O}{-}CH_2CH_3 + H{-}\overset{\oplus}{\underset{H}{O}}{-}H$

Another acid-base reaction converts the protonated ether to an ether by transferring a proton to a molecule of water (or to another molecule of the alcohol).

Only one combination of alkythalide and alkoxide is appropriate for the preparation of each of the following ethers by Willianson ether synthesis. What is the correct combination in each case ?

3. Form alkenes

(a) By addition of alcohols in alkenes

When alcohol is added to alkenes in presence of acid, we get ethers.

General reaction

(I) $>C=C< \xrightarrow{H_2SO_4}$ carbocation

(II) Carbocation + alcohol $\longrightarrow$ ether

e.g. (I) $Me_2C=CH_2 + H^{\oplus}(H_2SO_4) \longrightarrow Me_3C^{\oplus}$

(II) $Me_3C^{\oplus} + EtOH \rightleftharpoons Me_3C-\overset{\oplus}{O}(H)-Et \xrightarrow{-H^{\oplus}} Me_3COEt$

(b) Alkoxymercuration - demercuration

$>C=C< \xrightarrow[ROH]{Hg(OAc)_2} -\overset{|}{C}(AcOHg)-\overset{|}{C}(:\ddot{O}-H)- \xrightarrow{NaBH_4} -\overset{|}{C}(H)-\overset{|}{C}(OR)-$

mercurial ether

e.g.

(i) $RCH=CH_2+R'OH \xrightarrow[(ii)\ NaBH_4]{(i)\ Hg(OCOCF_3)_2} RCH(OR')CH_3$

(ii) $CH_2=CHCH_3+CH_3CH(OH)CH_3 \xrightarrow[(ii)\ NaBH_4]{(i)\ Hg(OCOCF_3)_2} CH_3-\underset{CH_3}{\overset{|}{C}H}-O-\underset{CH_3}{\overset{|}{C}H}-CH_3$

(iii) $CH_3CH=CHCH_3+CH_3CH(OH)CH_2CH_3 \xrightarrow[(ii)\ NaBH_4]{(i)\ Hg(OCOCF_3)_2} CH_3-\underset{CH_3}{\overset{|}{C}H}-CH_2-CH-O-\underset{CH_3}{\overset{|}{C}H}-CH_2-CH_3$

Reactions of ethers

1. With HX

General reaction

$R-\ddot{O}(R')-H \overset{\oplus}{\underset{\ominus}{X}} \rightleftharpoons R-\overset{\oplus}{O}(H)-R' \longrightarrow \underset{\text{alkyl halide}}{X-R} + :\ddot{O}(H)-R' \xrightarrow{HX} X-R + X-R'$

e.g. (i) $CH_3CH_2CH_2CH_3 \xrightarrow{HBr} 2CH_3-CH_2Br$

2. Reaction with sulphuric acid

Ethers dissolve in concentrated solutions of strong inorganic acids to from oxonium salts, i.e. ether behave as bronsted Lowry bases.

$R_2O + H_2SO_4 \underset{}{\overset{conc.H_2SO_4}{\rightleftharpoons}} (R-\overset{\oplus}{O}(H)-R)HSO_4^{\ominus} \xrightarrow{\Delta} R-OH + \underset{\text{alkyl hydrogen sulphate}}{R-O-SO_2OH}$

When heated with dilute H_2SO_4

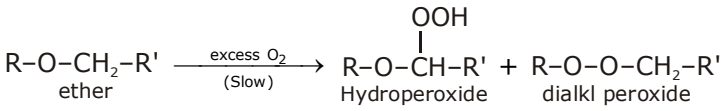
$R_2O + H_2SO_4 \xrightarrow{\Delta} 2ROH$

e.g. $C_2H_5OC_2H_5 + H_2SO_4 \xrightarrow{\Delta} C_2H_5OH + C_2H_5OHSO_4 \xrightarrow[\Delta]{H_2O} C_2H_5OH + H_2SO_4$

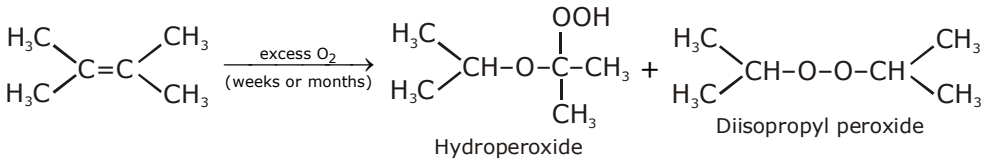
3. Autoxidation of ethers :

When ethers are stored in the presence of atmospheric oxygen, they slowly oxidize to produce hydroperoxides and dialkyl peroxides, both of which are explosive. Such a spontaneous oxidation by atmospheric oxygen is called an autoxidation.

General reaction



Ex. (i)



(ii) $CH_3CH_2–O–CH_2CH_3 \xrightarrow{h\upsilon}$ $CH_3–\underset{\displaystyle OOH}{\underset{|}{CH}}–O–CH_2CH_3$

Diethyl ether — 1-Ethoxyethyl hydroperoxide

4. Reaction with acid chlorides and anhydrides

Reagent : $ZnCl_2$, $AlCl_3$ etc.

General reaction (i) $R–O–R + R–CO–Cl \xrightarrow{AlCl_3} R–Cl + RCOOR$

Mech.

$$RCOCl + AlCl_3 \rightleftharpoons RCO^+ + AlCl_4^-$$

$$R'–\underset{\displaystyle R''}{\underset{|}{O}} + RCO^+ \longrightarrow R'–\overset{+}{\underset{\displaystyle R''}{\underset{|}{O}}}–COR \longrightarrow RCOOR' + \overset{\oplus}{R''} \xrightarrow{AlCl_4^{\ominus}} R''Cl + AlCl_3$$

e.g. $C_2H_5OC_2H_5 + CH_3COCl \xrightarrow[ZnCl_2]{\text{Anhydous}} C_2H_5Cl + CH_3COOC_2H_5$

(ii) $R_2O + \underset{\text{acid anhydride}}{(CH_3CO)_2O} \xrightarrow{ZnCl_2} 2CH_3COOR$

e.g. $C_2H_5OC_2H_5 + (CH_3CO)_2O \xrightarrow[AlCl_3]{\text{anhydrous}} 2CH_3COOC_2H_5$

5. Reaction with carbon monoxide :

Ether react with CO at 125-180°C and at a pressure of 500 atm, in the presence of BF_3 plus a little water.

$$R_2O + CO \xrightarrow[125–180^\circ C]{BF_3,\ 500\,atm} RCOOR$$

6. Reaction with halogens :

When treated with chlorine or Br, ether undergo substitution, the extent of which depends on the conditions.

$$CH_3CH_2OCH_2CH_3 \xrightarrow[h\upsilon]{Cl_2} CH_3CHClOCH_2CH_3 \xrightarrow[h\upsilon]{Cl_2} CH_3CHClOCHClCH_3$$

in presence of light

$$(C_2H_5)_2O \xrightarrow[h\upsilon]{Cl_2} \underset{\text{Perchloro diethyl ether}}{(C_2Cl_5)_2O}$$

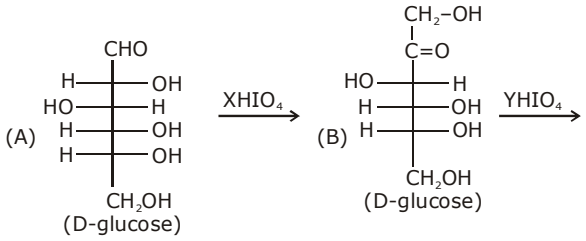
Mech.

The reaction proceeds by a free–radical mechanism, and α–substitution occurs readily because of resonance stabilization of the intermediate radical

$$R'\ddot{O}–CH_2R'' \xrightarrow{Cl^\bullet} R'\ddot{O}–\dot{C}HR'' \longleftrightarrow R'\dot{O}=CHR \xrightarrow{Cl_2} R'\ddot{O}–\dot{C}HClR'' + Cl^\bullet, \text{ etc.}$$

EXERCISE – I OBJECTIVE PROBLEMS (JEE MAIN)

1.



x & y are moles of HIO_4 consumed is above reaction.

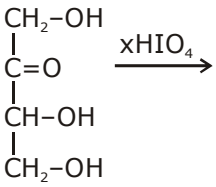
(i) Value of x inabove reaction is -
(A) 2 (B) 3
(C) 4 (D) 5

(ii) Sum of x + y is -
(A) 8 (B) 9
(C) 10 (D) 11

(iii) Mole of HCHO formed in (A) is -
(A) 1 (B) 2
(C) 3 (D) 4

Sol.

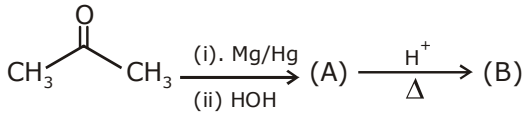
2.



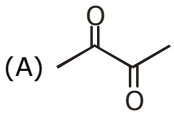
x is moles of HIO_4 consumed
(A) x = 3 (B) x = 2
(C) x = 4 (D) x = 1

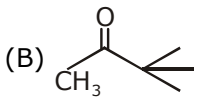
Sol.

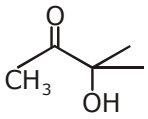
3.

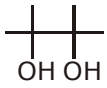


Product (B) is -

(A) 

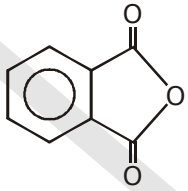
(B) 

(C) 

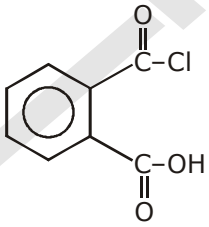
(D) 

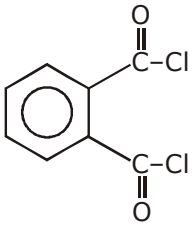
Sol.

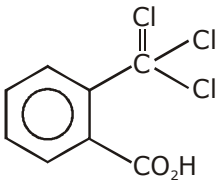
4.

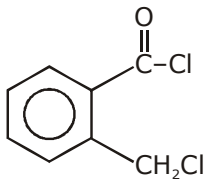


$\xrightarrow{PCl_5}$ (A); Product (A) is -

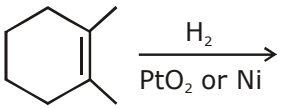
(A) 

(B) 

(C) 

(D) 

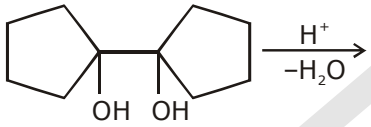
Sol.

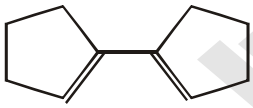
5. 

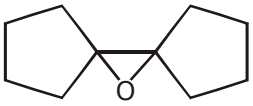
Product of above reaction is obtained by
(A) racemic mixture
(B) Diastereomers
(C) Meso
(D) Optically-active product

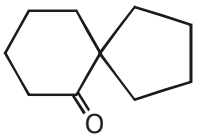
Sol.

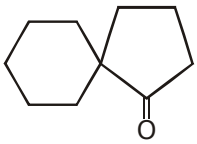
6. The structure of the product formed in the reaction given below is -



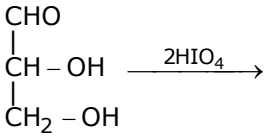
(A) 

(B) 

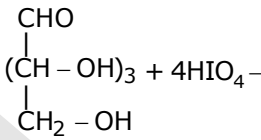
(C) 

(D) 

Sol.

7.  , Products obtained in the above reaction are -
(A) HCHO, HCO_2H
(B) HCHO, $2HCO_2H$
(C) CO_2, $2HCO_2H$
(D) CO_2, HCHO, HCO_2H

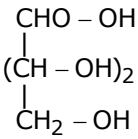
Sol.

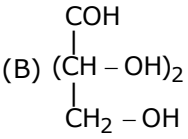
8.  , Products obtained are

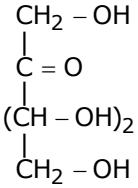
Aldo pentose
(A) $4HCO_2H$, HCHO (B) $4CH_2O$, HCO_2H
(C) CO_2, 4HCHO
(D) CO_2, $3HCO_2H$, HCHO

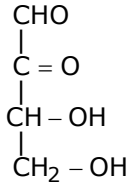
Sol.

9. Which of the following compound gives 2HCHO, CO_2, $2HCO_2H$ when oxidisized by periodic acid

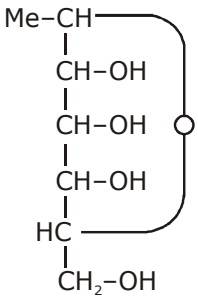
(A) 

(B) 

(C) 

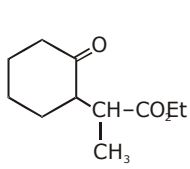
(D) 

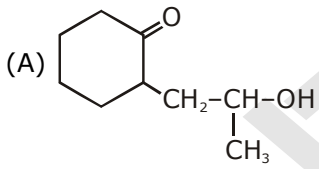
Sol.

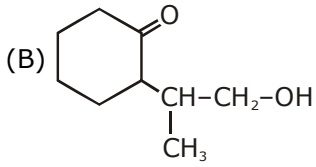
10.  $\xrightarrow{xHIO_4}$, What is the maximum value of (x) ?

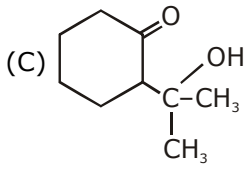
(A) 1 (B) 2
(C) 3 (D) 4

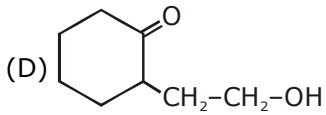
Sol.

11.  $\xrightarrow[H^+]{CH_2OH\ CH_2OH}$ (A) $\xrightarrow{LiAlH_4}$ (B) $\xrightarrow{H_2O^{\oplus}}$ (C)

(A) 

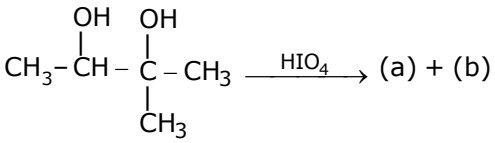
(B) 

(C) 

(D) 

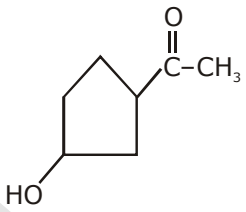
Sol.

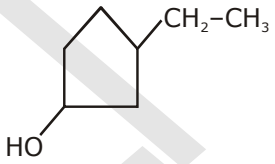
12. In the given reaction :



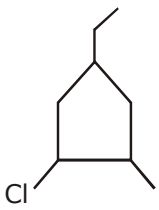
(a) and (b) respectively be -
(A) CH_3CHO and CH_3CHO
(B) CH_3COCH_3 and CH_3CHO
(C) CH_3COCH_3 and CH_3COCH_3
(D) CH_3COOH and CH_3COCH_3

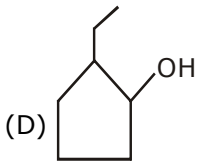
Sol.

13.  $\xrightarrow[HCl]{Zn(Hg)}$ (A); Identify the A.

(A) 

(B) 

(C) 

(D) 

Sol.

14. $Ph-CH_2-Cl \xrightarrow{KCN} (A) \xrightarrow{H_3O^{\oplus}} (B)$

$\xrightarrow{CH_3-{}^{18}OH,\ conc.H_2SO_4,\ \Delta} (C)$

product (C) is -

(A) $Ph-CH_2-C(=O^{18})-O-CH_3$

(B) $Ph-C(=O)-O^{18}-CH_3$

(C) $Ph-CH_2-C(=O)-O^{18}-CH_3$

(D) $Ph-CH_2-C(=O^{18})-O-CH_3$

Sol.

15. $Ph-C(=O)-CH_2-C(=O)-O-Et \xrightarrow{H_3O^{\oplus}} (A) \xrightarrow[\Delta]{} (B)$

Product (B) is -

(A) $Ph-C(=O)-H$ (B) $Ph-C(=O)-CH_3$

(C) $Ph-CH_2-C(=O)-OH$ (D) $Ph-CO_2H$

Sol.

16. $R-C(=O)-O-H+R_1-OH \underset{}{\overset{H^{\oplus}}{\rightleftharpoons}} R-C(=O)-O-R,$

In above esterification reaction rate of reactin is maximum, when R_1-OH is -

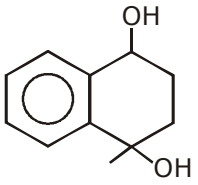
(A) 1º alcohol

(B) 3º alcohol

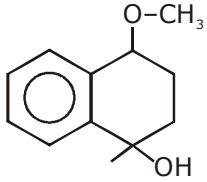
(C) 2º alcohol

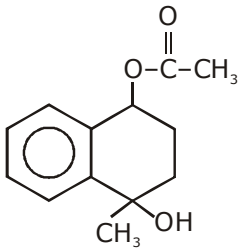
(D) CH_3OH

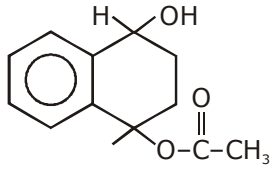
Sol.

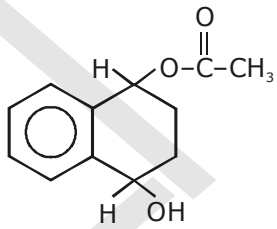
17.  $\xrightarrow[H^{\oplus}]{CH_3CO_2H(1mole)}$ (A) product

(A) is -

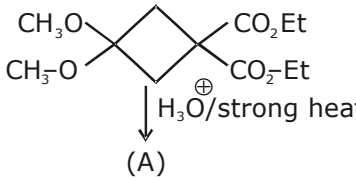
(A) 

(B) 

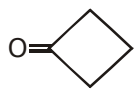
(C) 

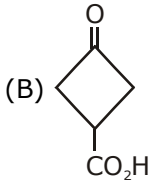
(D) 

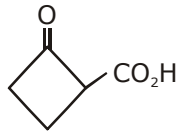
Sol.

18. 

is -

(A) 

(B) 

(C) 

(D) 

Sol.

19. $R_1-\overset{O}{\overset{\|}{C}}-O-H + R-OH \overset{H_3O^{\oplus}}{\rightleftharpoons} R_1-\overset{O}{\overset{\|}{C}}-O-R- + H_2O$

In above esterification reaction rate of reaction maximum when -

(A) $R_1 = -CH_3$ (B) $R_1 = -CH_2-CH_3$

(C) $R_1 = -CH(CH_3)_2$ (D) $R_1 = -C(CH_3)_3$

Sol.

20. $Ph-\overset{O}{\overset{\|}{C}}-\overset{18}{C}-CH_3 \overset{H_3O^{\oplus}}{\rightleftharpoons}$

O^{18} is present in -

(A) Carboxylic acid (B) Alcohol

(C) Water (D) Cannot predict

Sol.

21. $Ph-\overset{O}{\overset{\|}{C}}-O-CH_3 \xrightarrow{H_2O/HO^{\ominus}}$

Above reaction is known as -

(A) Esterification (B) saponification

(C) Transesterification (D) Acidic hydrolysis

Sol.

22. $CH_3\overset{18}{O}H \xrightarrow{Na}$ (A) + B (gas)

$CH_3-\overset{O}{\overset{\|}{C}}-O-CH_3 \xrightarrow{(A)}$ (C)

Product (C) of above reaction is -

(A) $CH_3-\overset{O^{18}}{\overset{\|}{C}}-O-CH_3$ (B) $CH_3-\overset{O}{\overset{\|}{C}}-\overset{18}{O}-CH_3$

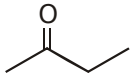
(C) $CH_3-\overset{O^{18}}{\overset{\|}{C}}-\overset{18}{O}-CH_3$ (D) $CH_3-\overset{O}{\overset{\|}{C}}-O-CH_3$

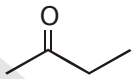
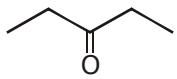
Sol.

23. $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-O-Et \xrightarrow{NaOEt}$ (A)

$\xrightarrow{CH_3I}$ (B) $\xrightarrow[\Delta]{H_3O^{\oplus}}$ (C)

Product (C) is -

(A)  (B) 

(C)  (D) 

Sol.

24. $R-\underset{(d\ \&\ l)\ racemic}{\overset{O}{\overset{\|}{C}}}-Cl + \underset{(d)}{R-O-H} \xrightarrow[Pyridine]{}$

Product of above reaction is -

(A) Enantiomer (B) Racemic

(C) Diastereomers (D) Meso

Sol.

25. $Ph-\overset{O}{\overset{\|}{C}}-O-H + CH_3-O^{18}H \rightleftharpoons (X) + H_2O$

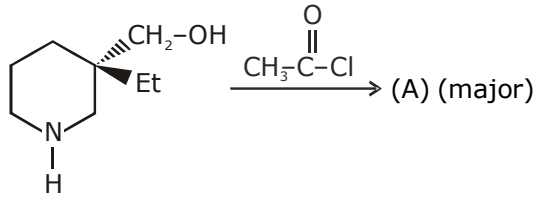
(A) X = $Ph-\overset{O}{\overset{\|}{C}}-O^{18}-CH_3$ (Trans esterification)

(B) X = $Ph-\overset{O}{\overset{\|}{C}}-O^{18}-CH_3$ (esterification reaction)

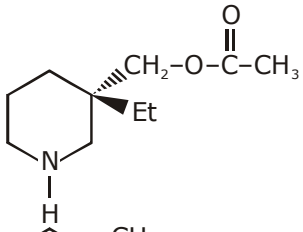
(C) X = Ph–C(=O)–O^{18}–CH_3(Saponification)

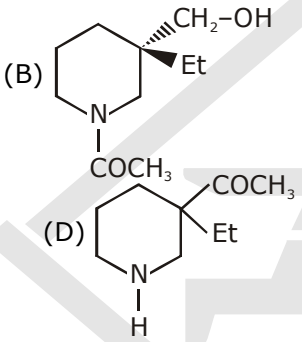
(D) X=Ph–C(=O)–O–CH_3 (Hydrolysis)

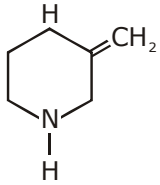
Sol.

26. 

(A) (major)

(A) 

(B) 

(C) 

(D)

Sol.

27. Which of the following compound reduces by DIBAL-H ?

(A) CH_3–C(=O)–OH (B) CH_3–C≡N

(C) CH_3–C(=O)–O–Et (D) All

Sol.

28. Which of the following compound reduces by $NaBH_4$?

(A) CH_3–C(=O)–OH (B) CH_3–NO_2

(C) CH_3–C(=O)–O–Et (D) CH_3–C(=O)–Cl

Sol.

29. Which of the following compounds not reacts with NaOH ?

(A) HC≡CH (B) EtOH

(C) $H_2C=CH_2$ (D) All

Sol.

30. EtOH+CH_3–C(=O)–O–C(=O)–CH_3 ⟶

In above reaction molecular weight of alcohol increases by

(A) 22 (B) 32

(C) 42 (D) 52

Sol.

31. N-Ethyl pthalimide oin hydrolysis gives -

(A) Methyl alcohol (B) Ethyl amine

(C) Dimethyl amine (D) Diethyl amine

Sol.

32. Which of the following is acetylation reaction

(A) EtOH $\xrightarrow[\Delta]{H^+}$

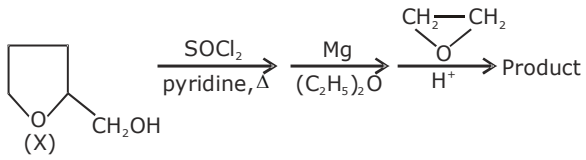
(B) EtOH + CH_3–C(=O)–O–C(=O)–CH_3

(C) EtOH + H – CL ⟶

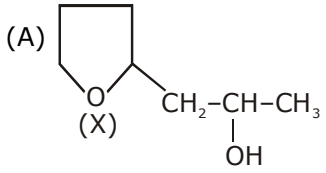
(D) $EtO^{\ominus}$ + CH_3 – CH_2 – Cl ⟶

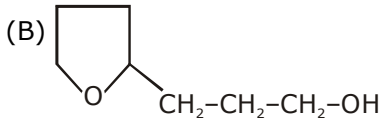
Sol.

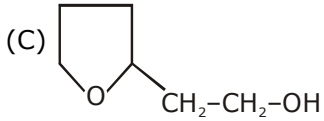
EXERCISE – II OBJECTIVE PROBLEMS (JEE ADVANCED)

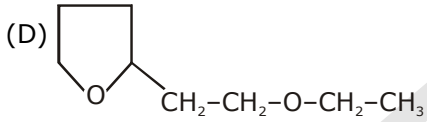
1. 

Product of the reaction is -

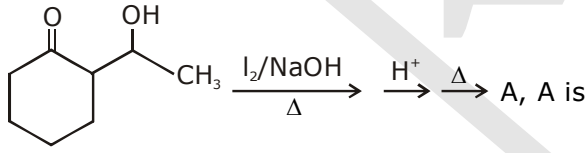
(A) 

(B) 

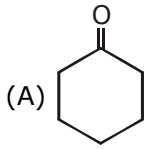
(C) 

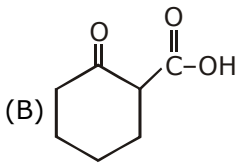
(D) 

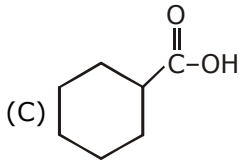
Sol.

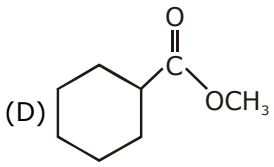
2. 

A, A is -

(A) 

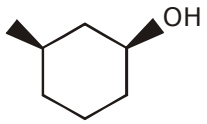
(B) 

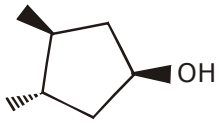
(C) 

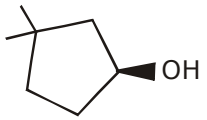
(D) 

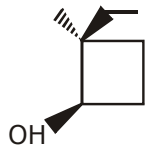
Sol.

3. $AC_7H_{14}O$ optically active alcohol is oxidized by jones' reagent to an optically inactive (achiral) ketone. Which of the following compounds meets these facts ?

(A) 

(B) 

(C) 

(D) 

Sol.

4. Glycol on treatment with PI_3 mainly gives -
(A) Ethylene (B) Ethylene iodide
(C) Ethyl iodide (D) Ethane

Sol.

5. Ethanol on reaction with acetic anhydride gives
(A) Acetic ester (B) Formic ester
(C) Ethaoic acid
(D) Acetic ester and Ethanoic acid both

Sol.

6. A compound 'X' with molecular formula C_3H_8O can be oxidised to a compound 'Y' with the molecular formula $C_3H_6O_2$, 'X' is most likely to be -
(A) Primary alcohol
(B) Seconary alcohol
(C) Aldehyde
(D) Ketone

Sol.

7. Phenol with Hinsberg's reagent gives -
(A) Sulphone (B) Sulphanilic acid
(C) Sulphonic ester (D) Sulphonal

Sol.

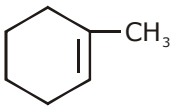
8. Glycerol $\xrightarrow[\Delta]{KHSO_4}$ A $\xrightarrow{LiAH_4}$, A and B are
(A) Acrolein, allyl alcohol
(B) Glycerl sulphate, acrylic acid
(C) Allyl alcohol, acrolein
(D) Only acrolein (B is not formed)

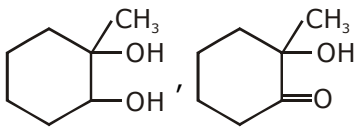
Sol.

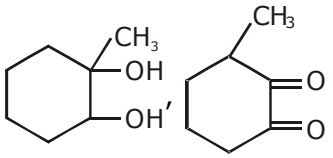
9. Phenol $\xrightarrow[(ii)\ CO_2/140^oC]{(i)\ NaOH}$ A $\xrightarrow{H^+/H_2O}$ B $\xrightarrow[CH_3COOH\Delta]{Al_2O_3}$ C

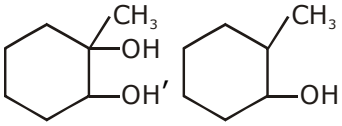
In this reaction, the end product C is -
(A) Salicylaldehyde (B) salicylic acid
(D) Phenyl acetate (D) aspirin

Sol.

10.  $\xrightarrow[alkaline\ KnO_4]{cold}$ A $\xrightarrow[AcOH]{CrO_3}$ B, A and B are -

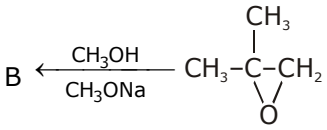
(A) 

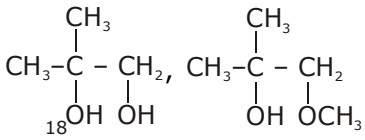
(B) 

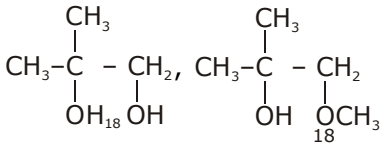
(C) 

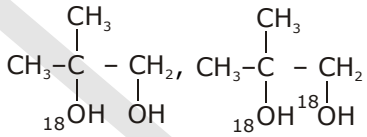
(D) no formation of A and B

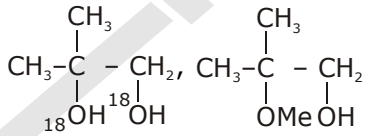
Sol.

11.  A, A and B are -

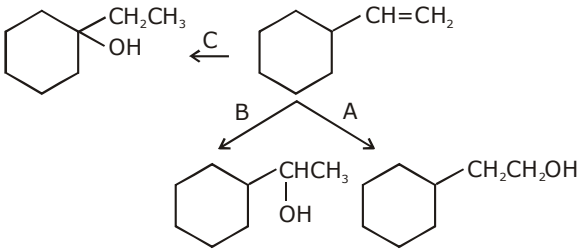
(A) 

(B) 

(C) 

(D) 

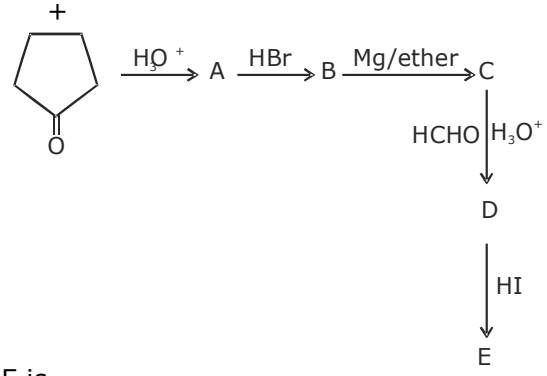
Sol.

12. 

Select schemes A, B, C out of -
I. acid catalysed hydration
II. HBO
III. Oxymercuration-demercuraton
(A) I in all cases (B) I, II, III
(C) II, III, I (D) III, I, II

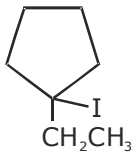
Sol.

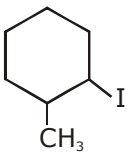
13. CH_3MrBr +

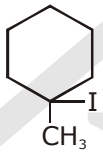


E is -

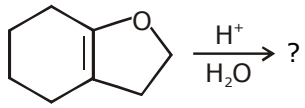
(A) 

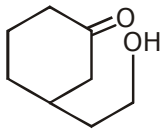
(B) 

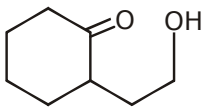
(C) 

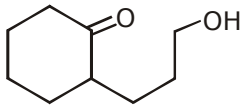
(D) 

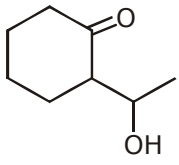
Sol.

Q.14 

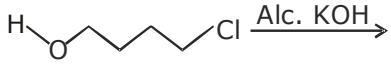
(A) 

(B) 

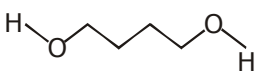
(C) 

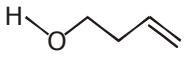
(D) 

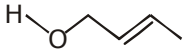
Sol.

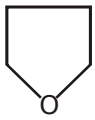
15. 

Major product is -

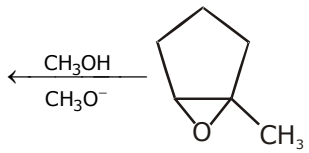
(A) 

(B) 

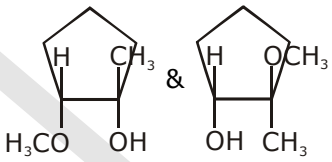
(C) 

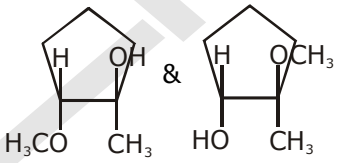
(D) 

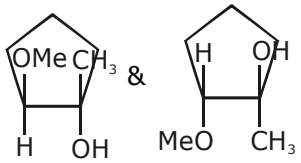
Sol.

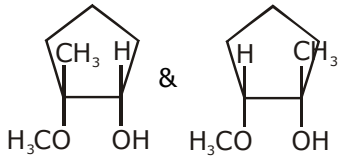
16. (A) 

(B) A & B are -

(A) 

(B) 

(C) 

(D) 

Sol.

17. $CH_2 = \underset{\underset{OH}{|}}{CHCHCH_2CH_2OH} \xrightarrow{MnO_2}$ A, A is -

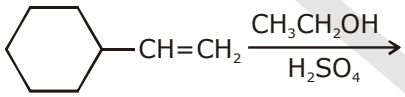
(A) $CH_2 = CHC(=O)CH_2CH_2OH$

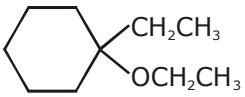
(B) $CH_2 = \underset{\underset{OH}{|}}{CHCCH_2CHO}$

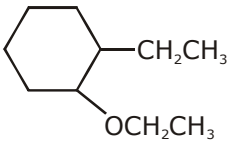
(C) $CH_2 = CHC(=O)CH_2CHO$

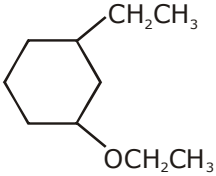
(D) $CH_2=CHC(=O)CH_2C(=O)OH$

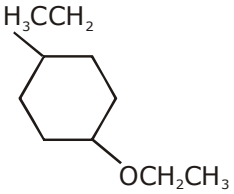
Sol.

18.  find out the product :

(A) 

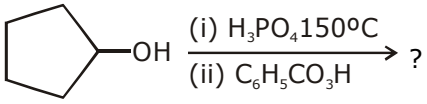
(B) 

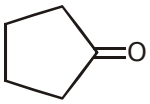
(C) 

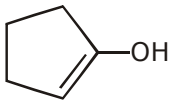
(D) 

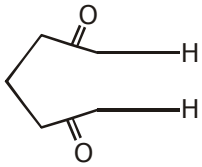
Sol.

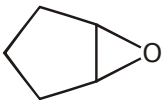
19. What will be the chief productg from the following reaction sequence ?



(A) 

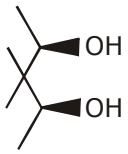
(B) 

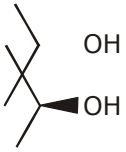
(C) 

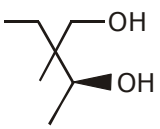
(D) 

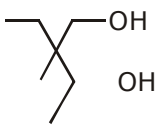
Sol.

20. A chiral $C_7H_{16}O_2$ diol is oxidized by PCC in CH_2Cl_2 to an achiral $C_7H_{12}O_2$ compound. Which of the following wuld satisfy these facts?

(A) 

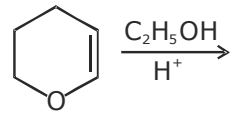
(B) 

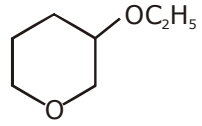
(C) 

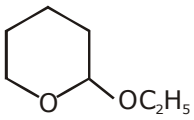
(D) 

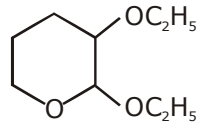
Sol.

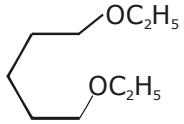
21. Which of the following is the product from ethanol addition to dihydropyran (shown on the left below) ?



(A) 

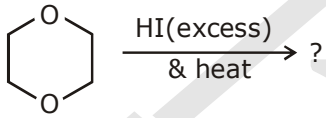
(B) 

(C) 

(D) 

Sol.

22. What product (s) are expected from the following reaction ?



(A) $2CH_3CH_2I$ (B) $2ICH_2CH_2OH$
(C) $2iCH_2CH_2$
(D) $CH_3CH_2I + CH_3CH_2OH$

Sol.

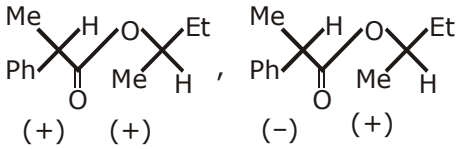
23. Which of the following reagents would be best for oxidizing a 1º-alcohol to an aldehyde ?
(A) H_3PO_4
(B) PCC in CH_2Cl_2
(C) Jonew's reagent (H_2CrO_4)
(D) OsO_4

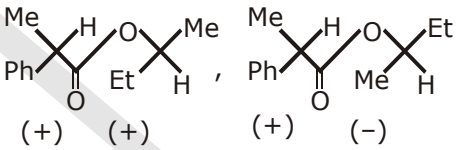
Sol.

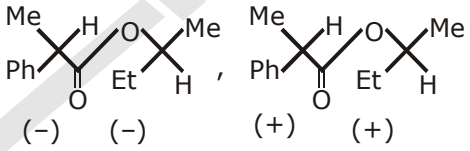
24. A water soluble $C_6H_{14}O_2$ compound is oxidized by lead tetraacetate (or periodic acid) to a single C_3H_6O carbonyl compound. Which of the following would satisfy this fact ?
(A) meso-2, 3-dimensthoxybutane
(B) 1,2-diethoxyethane
(C) meso-2,5-hexanediol
(D) meso-3,4-hexanediol

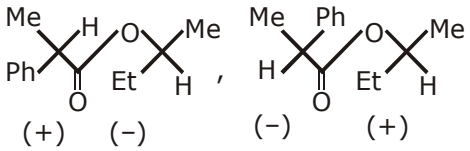
Sol.

25. A racemic mixture of (±) 2-phenyl propanoic acid on esterificaton with (+) 2-butanol gives two esters. Mention the sterochemistry of two esters formed -

(A) 

(B) 

(C) 

(D) 

Sol.

26. Compound which gives alcohol on reduction is/ are (When reacts with $LiAH_4$)

(A) $Me-\overset{\overset{O}{\|}}{C}-Cl$

(B) $Me-\overset{\overset{O}{\|}}{C}-NH_2$

(C) $Me-CH-CH_2$ (epoxide)

(D) $Me-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-Me$

Sol.

27. Which of following compound undergo acidic hydrolysis.

(A) $CH_3-C\equiv N$

(B) $CH_3-\overset{\overset{O}{\|}}{C}-O-Et$

(C) $CH_3-\overset{\overset{O}{\|}}{C}-Cl$

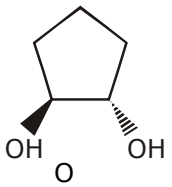
(D) $CH_3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3$

Sol.

28. Which can be cleaved by HIO_4 ?

(A) $CH_3CH_2\overset{\overset{O}{\|}}{C}CH_2\overset{\overset{O}{\|}}{C}CH_3$

(B) $CH_3\underset{\underset{OH}{|}}{CH}\overset{\overset{O}{\|}}{C}CH_2CH_3$

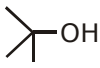
(C) 

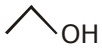
(D) $CH_3\overset{\overset{O}{\|}}{C}CH_2\underset{\underset{OH}{|}}{CH}CH_2\overset{\overset{O}{\|}}{C}CH_3$

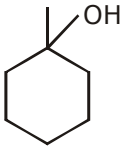
Sol.

29. Which of the following alcohol can not be oxidized by $KMnO_4$:

(A) 

(B) 

(C) 

(D) 

Sol.

30. Which of the following reaction esterification ?

(A) EtOH + Acetic anhydride $\longrightarrow$

(B) EtOH + $CH_3CO_2H \xrightarrow[\Delta]{H^+}$

(C) EtOH – $CH_3-\overset{\overset{O}{\|}}{C}-Cl$

(D) None

Sol.

31. CH_3-

$\underset{\underset{O}{\diagdown\diagup}}{CH-CH_2} \xrightarrow{CH_3C\equiv C} (X) \xrightarrow{CH_3I} (Y) \xrightarrow{H_2/Pd/BaSO_4} (Z)$

Identify X, Y, Z :

(A) Y is $CH_3-\underset{\underset{O-CH_3}{|}}{CH}-CH_2C\equiv CCH_3$

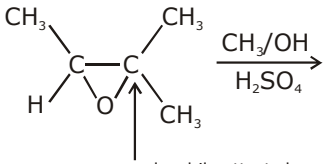
(B) Y is $CH_3-CH_2-\underset{\underset{CCH_3}{|}}{CHC}\equiv CCH_3$

(C) Z is $CH_3-\underset{\underset{O-CH_3}{|}}{CH}-CH_2-CH=CH-CH_5$

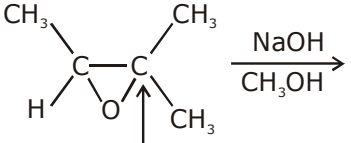
(D) X is $CH_3-\underset{\underset{O^{\Theta}}{|}}{CHCH_2C}\equiv CCH_3$

Sol.

32. Which is/are corect statement ?

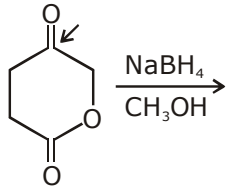
(A) 

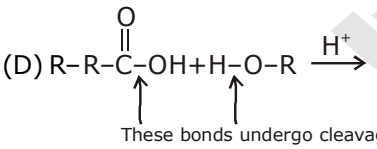
nucleophile attacts here when epoxy linkage is cleaved

(B) 

nucleophile attacts here when epoxy linkage is cleaved

(C) This is only affected in reduciton to 2º alcohol



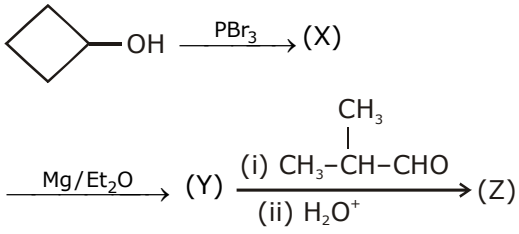
(D) 

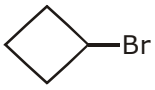
These bonds undergo cleavage in the reaction

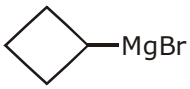
Sol.

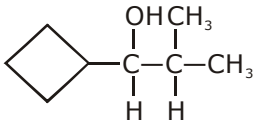
33. 3-methyl-3-hexanol can be prepared by -
(A) CH_3MgI and 3-hexanone, followed by hydrolysis
(B) C_2H_5 MgI and 2-Pentanone, followd by hydrolysis
(C) C_3H_7MgI and 2-butananone, followd by hydrolysis
(D) C_4H_9 MgI and propanon, followed by hydrolysis

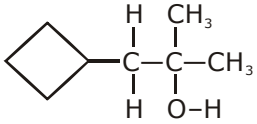
Sol.

34. 

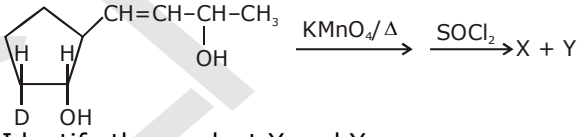
(A) X is 

(B) Y is 

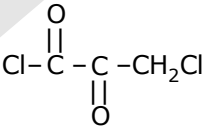
(C) Z is 

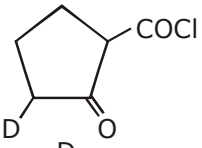
(D) Z is 

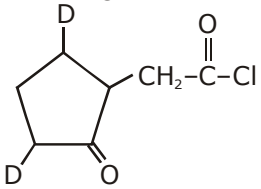
Sol.

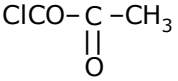
35. 

Identify the product X and Y.

(A) X is 

(B) X is 

(C) Y is 

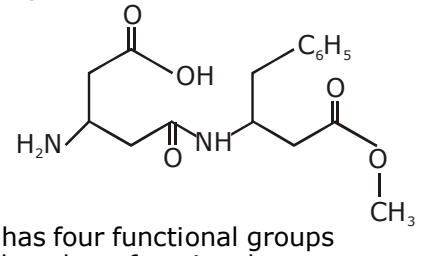
(D) Y is 

Sol.

36. Which one of the following alcohols can be oxidised by K_2CrO_4 ?
(A) Ethanol (B) Tert butyl alcohol
(C) Isopropyl alcohol (D) Allyl alcohol

Sol.

37. Asparmatge, an artificial sweetener is a peptide and has the following structure. Which of the following is correct about the molecule ?

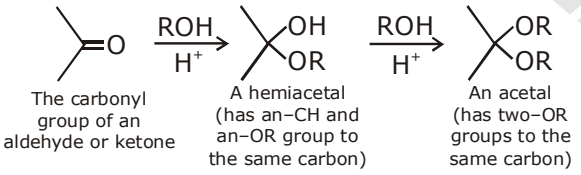


(A) It has four functional groups
(B) It has three functional groups
(C) on hydrolysis it produces only one amino acid
(D) on hydrolysis it produces a mixture of amino acids

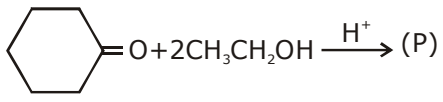
Sol.

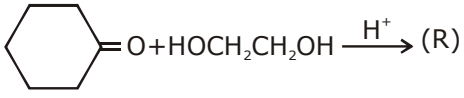
Comprehansion : (Q.38 to Q.40) :

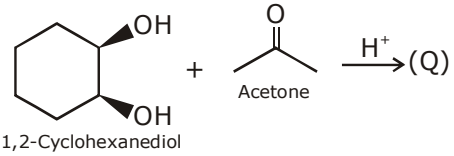
Aldehydes and ketones react with oine molecule of analcohol to form compounds called hemiacetals, in which there is one hydroyl group and one either-like group. Reaction of a hemiacetal with a second molecule of alcohol gives an acetal and a molecule of water. We study this reaction



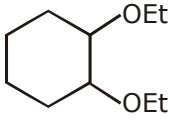
Draw structural formulas for the hemicetal and acetal formed from these reagents. The stoichiometry of each reaction is given in the problem.

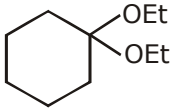
(A) 

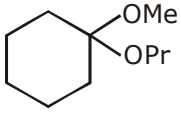
(B) 

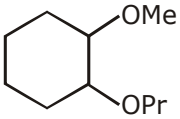
(C) 

38. Product P is -

(A) 

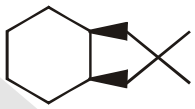
(B) 

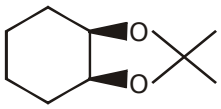
(C) 

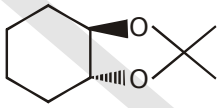
(D) 

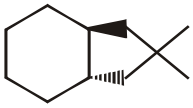
Sol.

39. Product Q is -

(A) 

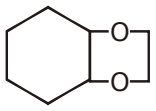
(B) 

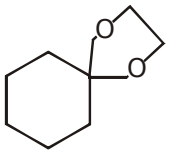
(C) 

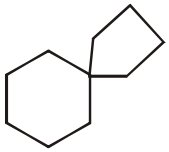
(D) 

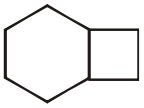
Sol.

40. Product R is -

(A) 

(B) 

(C) 

(D) 

Sol.

EXERCISE – III OBJECTIVE PROBLEMS (JEE ADVANCED)

1. How can you convert PhCH = $CHCH_3$ to -
(i) $PhCH{=}CHCO_2H$
(ii) $PhCH{=}CHCH_2CH_3$
(iii) $PhCH_2CH_2CH_2CH_3$
(iv) $PhCH{=}CHCH(OH)CH_3$
(V) $PhCH_2CH_2COCH_3$

Sol.

2. What reagents could you use for the following conversions
(a) $MeCO(CH_2)_2CO_2Et \rightarrow MeCHOH(CH_2)_2CO_2Et$
(b) $HO_2C(CH_2)_4COCl \longrightarrow HO_2C{-}(CH_2)_4CH_2OH$
(c) $O_2N(CH_2)_2CN \longrightarrow O_2N(CH_2)_2CH_2NH_2$
(d) $O_2N(CH_2)_2CH{=}CH_2 \longrightarrow H_2N(CH_2)_2CH{=}CH_2$
(e) $Me_2CHCOCl \longrightarrow Me_2CHCHO$
(f) $O_2N(CH_2)_3CHO \longrightarrow O_2N(CH_2)_3CH_2OH$
(g) $O_2N(CH_2)_2CH{=}CH_2 \longrightarrow O_2N(CH_2)_3CH_3$

Sol.

3. Outline a mechanism to account for different isomer formed when $Me_2C\text{—}CH_2$ (O) reacts with CH_3OH in acidic and in basic medium.

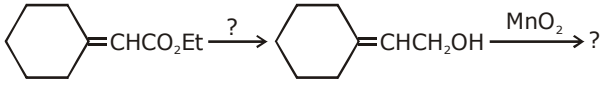
Sol.

4. Differentiate :
(a) 1-Hexanol and 1-chlorohexane
(b) Diethyl ether and n-butanol
(c) Diethyl ether and n-pentane

Sol.

5. Complete the following equations & comment
(i) $MeOEt \xrightarrow{HI} ?$ (ii) $Et_2O \xrightarrow{Na}$

Sol.

6. Complete the following equations :
(i) $n{-}C_3H_7{-}CO_2H \longrightarrow n{-}C_4H_9OH$
(ii) $Me_2CO + EtMgI \longrightarrow ? \xrightarrow{H^+} ?$
(iii) $EtCO_2Et + 2MeMgI \longrightarrow ? \xrightarrow{H_2O} ?$
(iv) 

Sol.

7. t-butyl alcohol reacts less rapidly with metallic sodiumthan thepriamry alcohol. Explain why ?

Sol.

8. Diethyl ether behaves as base. Why ?

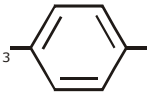
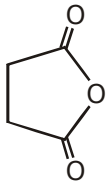
Sol.

9. Sometimes explosion occurs during distillation of ether sample. Give the reason.

Sol.

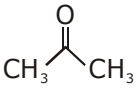
10. Ethyl alcohol reacts with HI but not with HCN. Explain why ?

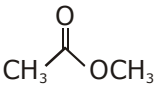
Sol.

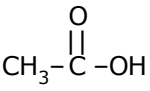
11. Write the structure of the principal organic product formed in the reaction of 1-propanol with each of the following reagents :
(i) Potassium dichromate ($K_2Cr_2O_7$) in aqueous sulfuric acid, heat
(ii) Acetic acid $CH_3\overset{O}{\overset{\|}{C}}OH$ in the presence of disolved hydrogen chloride.
(iii)  in the presence of pyridine
(iv) $C_6H_5\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}C_6H_5$ in the presence of pyridine
(v)  in the presence of pyridine

Sol.

12. **Column-I** **Column-II**

(A)  (P) Reduces by LAH

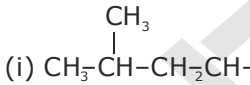
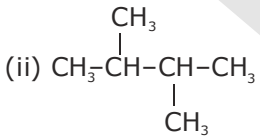
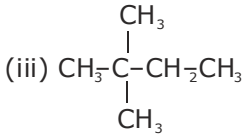
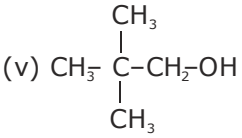
(B)  (Q) Reduce by $NaBH_4$

(C)  (R) Positive Iodoform

(D) (S) Reacts with Na to evolve H_2 gas

Sol.

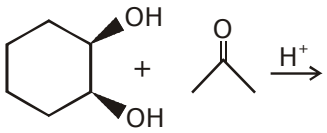
13. Match the following X, yZ ($C_5H_{12}O$) are isomeric alcohols on oxidation 'X' gives a given, Y gives acid and Z is not oxidised X gives positive I_2/ $OH^{\ominus}$ test. The activity order with HBr is Z > X > Y.

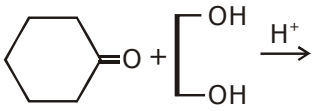
(X)	(i) 
(Y)	(ii) 
(Z)	(iii) 
	(iv) $CH_3-CH_2-CH_2-CH_2-OH$
	(v) 

Sol.

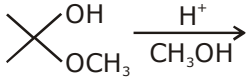
14. Match the following :

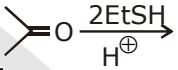
Column-I **Column-II**

(A)  (P) Product formed is known as Acetal

(B)  (Q) Product reacts with Nametalto evolve H_2 gas

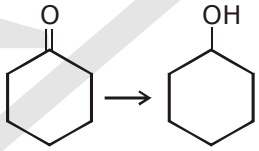
(C)  (R) Product when reacts with H_2| Ni formation of alkane takes place

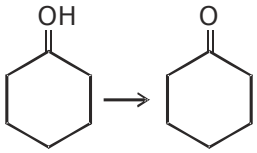
(D)  (S) Product when reacts with LAH No-reaction takes place

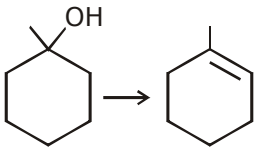
(E) 

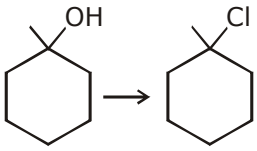
Sol.

15. **Column-I** **Column-II**

(A)  (P) H_2/Ni

(B)  (Q) PCC

(C)  (R) H_3PO_4/Δ

(D)  (S) conc. HCl

Sol.

16. Column-I

(A) $Ph-\underset{\underset{OH}{|}}{CH}-CH_3 \rightarrow Ph-\overset{\overset{O}{||}}{C}-CH_3$

(B) $Ph-CH_2-CH_2-OH \rightarrow Ph-CH_2-CO$

(C) $Ph-CH_2-CH_2-OH \rightarrow Ph-CH_2-CO_2H$

(D) $Ph-\underset{\underset{OH}{|}}{CH}-CH_3 \rightarrow Ph-CO_2H$

Column-II (Reagent used)

(P) hot alk.$KMnO_4$

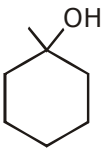
(Q) Cold. $KMnO_4$

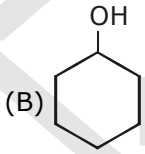
(R) CrO_3/CH_2Cl_2

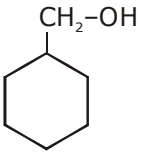
(S) Cu/300ºC

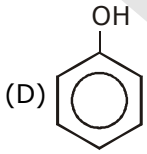
Sol.

17. Column-I

(A) 

(B) 

(C) 

(D) 

Column-II

(P) When reacts with $CrO_3H_2SO_4$ carboxylic acid will form.

(Q) Give positive test with $FeCl_3$.

(R) When reacts with HBr alkyl bromide will formed.

(S) When reacts with $K_2Cr_2O_7$ ketone will form.

(T) CrO_3 in anhydrous form (CH_3Cl_2) gives aldehyde

Sol.

18. Column-I

(A) $EtOH + CH_3-\overset{\overset{O}{||}}{C}-Cl \xrightarrow[\Delta]{\text{Pyridine}}$

(B) $EtOH + CH_3-\overset{\overset{O}{||}}{C}-O-\overset{\overset{O}{||}}{C}-CH_3 \xrightarrow[\Delta]{H^+}$

(C) $EtoH + CH_3-\overset{\overset{O}{||}}{C}-OH \xrightarrow[\Delta]{H^+}$

(D) $EtOH + EtOH \xrightarrow[\Delta]{H^+}$

Column-II

(P) Esterification reaction

(Q) Acetylation reaction

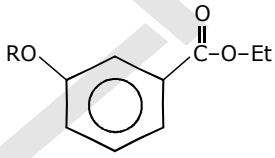
(R) Molecular formulaof alcohol increases by C_2H_2O

(S) Molecular weight of alcohol increases by28.

Sol.

19. Column-I

(A) $R-C\equiv N$

(B) 

(C) $Ph-\overset{\overset{O}{||}}{C}NH_2$

(D) $R-\overset{\overset{O}{||}}{C}-O-\overset{\overset{O}{||}}{C}-R$

Column-II

(P) When reacts with $H_3O^{\oplus}$, carboxylic acid will form

(Q) When reacts with $LiAlH_4$, 1º alcohol will form.

(R) When reacts with $LiAlH_4$, 1º amine will form.

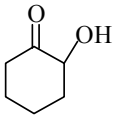
(S) When undergo alkaline hydrolysis salt of carboxylic will form

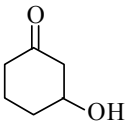
Sol.

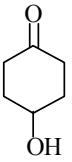
EXERCISE – IV PREVIOUS YEARS PROBLEMS

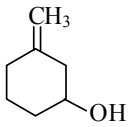
LEVEL – I JEE MAIN

Q.1 Maximum dehydration takes place that of – **[AIEEE-2002]**

(A) 

(B) 

(C) 

(D) 

Q.2 When CH_2=CH–COOH is reduced with $LiAlH_4$, the compound obtained will be – **[AIEEE-2003]**

(A) CH_3–CH_2–CH_2OH (B) CH_3–CH_2–CHO
(C) CH_3–CH_2–COOH (D) CH_2=CH–CH_2OH

Q.3 Among the following compounds which can be dehydrated very easily is - **[AIEEE-2004]**

(A) $CH_3CH_2CH_2CH_2CH_2OH$

(B) $CH_3\,CH_2\,CH_2\,\underset{\displaystyle CHCH_3}{\overset{\displaystyle OH}{|}}$

(C) $CH_3CH_2\overset{\displaystyle CH_3}{\underset{\displaystyle OH}{\overset{|}{\underset{|}{C}}}}\,CH_2\,CH_3$

(D) $CH_3\,CH_2\,\underset{\displaystyle CH_3}{\overset{\displaystyle CH}{|}}\,CH_2\,CH_2OH$

Q.4 For which of the following parameters the structural isomers C_2H_5OH and CH_3OCH_3 would be expected to have the same values ? (Assume ideal behaviour) **[AIEEE-2004]**

(A) Heat of vaporization
(B) Vapour pressure at the same temperature
(C) Boiling points
(D) Gaseous densities at the same temperature and pressure

Q.5 HBr reacts with CH_2 = CH – OCH_3 under anhydrous conditions at room temperature to give - **[AIEEE 2006]**

(A) $BrCH_2CHO$ and CH_3OH
(B) $BrCH_2$ – CH_2 – OCH_3
(C) H_3C – CHBr – OCH_3
(D) CH_3CHO and CH_3Br

Q.6 In the following sequence of reactions,

$CH_3CH_2OH \xrightarrow{P+I_2} A \xrightarrow[ether]{Mg} B \xrightarrow{HCHO} C \xrightarrow{H_2O}$ D, then compound 'D' is - **[AIEEE 2007]**

(A) butanal (B) n-butyl alcohol
(C) n-propyl alcohol (D) propanal

Q.7 A liquid was mixed with ethanol and a drop of concentrated H_2SO_4 was added. A compound with a fruity smell was formed. The liquid was **[AIEEE 2009]**

(A) HCHO (B) CH_3COCH_3
(C) CH_3COOH (D) CH_3OH

Q.8 From amongst the following alcohols the one that would react fastest with conc, HCl and anhydrous $ZnCl_2$, is – **[AIEEE 2010]**

(A) 1- Butanol
(B) 2- Butanol
(C) 2- Methylpropan -2-ol
(D) 2- Methylpropanol

Q.9 The main product of the following reaction is

$C_6H_5CH_2CH(OH)CH(CH_3)_2 \xrightarrow{conc.H_2SO_4} ?$

[AIEEE 2010]

(A) $H_5C_6CH_2CH_2\diagdown\!\!\diagup C=CH_2$ (with H_3C)

(B) H_5C_6, H on C=C, H, $CH(CH_3)_2$

(C) $C_6H_5CH_2$, H on C=C, CH_3, CH_3

(D) C_6H_5, H on C=C, $CH(CH_3)_2$, H

Q.10 Consider the following reaction :

$C_2H_5OH + H_2SO_4 \rightarrow$ Product

Among the following which one cannot be formed as a product under any conditions ? **[AIEEE 2011]**

(A) Ethylene (B) Acetylene
(C) Diethyl ether
(D) Ethyl-hydrogen sulphate

LEVEL – II JEE ADVANCED

1. 1-propanol & 2-propanol can be best distinguished by - **[JEE 2001]**
(A) oxidation with alkaline $KMnO_4$ followed by reaction Fehling solution
(B) Oxidation with acedic dichromate followed by reaction with Fehling solution
(C) Oxidation by heating with copper followed by reaction with Fehling solution
(D) Oxidatioin with concentrated H_2SO_4 followed by reaction with Fehling

Sol.

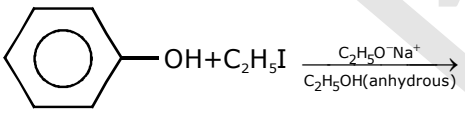
2. Identify the correct order of boiling point of the following compounds : **[JEE 2002]**

$CH_3\underset{1}{CH_2}CH_2OH$ $CH_3\underset{2}{CH_2}CHO$

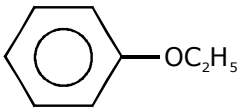
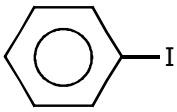
$CH_3CH_2\underset{3}{CH_2}COOH$

(A) 1 > 2 > 3 (B) 3 > 1 > 2
(C) 1 > 3 > 2 (D) 3 > 2 > 1

Sol.

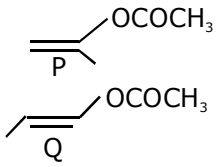
3. 

[JEE 2003]

(A)  (B) 

(C) $C_6H_5OC_6H_5$ (D) $C_2H_5OC_2H_5$

Sol.

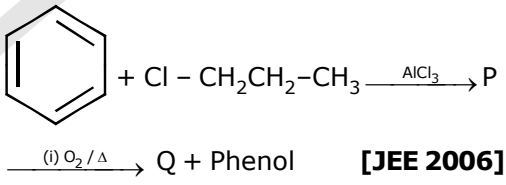
4. 

formed by P & Q can be differentiated by : **[JEE 2003]**
(A) 2, 4 DNP
(B) Lucas reagent ($ZnCl_2$) conc. HCl
(C) $NaHSO_3$
(D) Fehlings solution

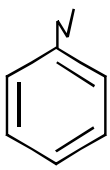
Sol.

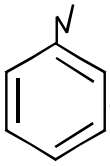
5. Reactn of entainomerically pure acid with 1 chiral carbon and racemic alcohol with 1 chiral carbon gives an ester which is - **[JEE 2003]**
(A) Meso
(B) Optically active mixture
(C) Racemic mixture
(D) Enationmerically pure

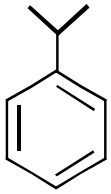
Sol.

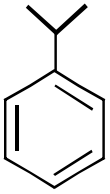
6. 

The major products P and Q are -

(A)  and CH_3CH_2CHO

(B)  and CH_3COCH_3

(C)  and CH_3COCH_3

(D)  and CH_3CH_2CHO

Sol.

7. **Satement-1 :** p-Hydroxybenzoic acid has a lower boiling point than o-hydroxybenzoic acid.
because
Statement-2 : o-Hydroxybenzoic acid has intramolecular hydrogen bonding.
[JEE 2007]
(A) Statement-1 is true, Statement-2 is True; Statement-2 is a correct explanation for Statement-1
(B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
(C) Statement-1 is True, Statement-2 is false.
(D) Statement-1 is False, Statement-2 is True.

Sol.

8. Cyclobutyl bromide on treatment with magnesium in dry ether forms an organometallic A. The organometallic reactw with ethanal to give an alcohol B after mild acidification. Prolonged treatment of alcohol B with an equivalent amount of HBr gives 1-bromo-methylcylopentane (C). Write the structures of A, B and explain how C is obtained from B.
[JEE 2001]

Sol.

9. Mention two esters produced when a racemic mixture of 2-phenyl propanoic acid is treated with (±) 2-butanol. What is the stereochemical relationship between these esters ?
[JEE 2003]

Sol.

10. $(X)C_5H_{13}N \xrightarrow[-N_2]{NaNO_2.HCl} (Y)$ (Tertiary alcohol + other products)
(Optically active)
Find X and Y. Is Y optically active ? Write the intermediate steps. **[JEE 2005]**

Sol.

11. **Column-I** **[IIT 2009]**
(A) $CH_3CH_2CH_2CN$
(B) $CH_3CH_2OCOCH_3$
(C) $CH_3-CH=CH-CH_2OH$
(D) $CH_3CH_2CH_2CH_2NH_2$(s)
Column-II
(P) Reduction with Pd-C/H_2
(Q) Reduction with $SnCl_2$/HCl
(R) Development of foul smell o n treatment with chloroform and alcoholic KOH
(S) Reduction with diisobutylauminium hydride (DiBAL-H)
(T) Alkaline hydrolysis

Sol.

Answers

Exercise-I

1.(i) D (ii) C (iii) A **2.** (A) **3.** (B) **4.** (B) **5.** (C) **6.** (C) **7.** (B) **8.** (A)

9. (C) **10.**(B) **11.**(B) **12.**(B) **13.**(B) **14.**(C) **15.**(B) **16.**(D) **17.**(B) **18.**(B)

19.(A) **20.**(B) **21.**(B) **22.**(B) **23.**(C) **24.**(C) **25.**(B) **26.**(B) **27.**(D) **28.**(D)

29.(D) **30.**(C) **31.**(B) **32.**(B)

Exercise-II

1.(B) **2.**(A) **3.**(C) **4.**(A) **5.**(D) **6.**(A) **7.**(C) **8.**(A) **9.**(D) **10.**(A) **11.**(A) **12.**(C)

13.(D) **14.**(B) **15.**(D) **16.**(B) **17.**(A) **18.**(A) **19.**(D) **20.**(B)

21.(B) **22.**(A) **23.**(B) **24.**(D) **25.**(A)

26.(A,C,D) **27.**(A,B,C,D) **28.**(B) **29.**(B,D) **30.**(A,B,C) **31.**(A,C,D) **32.**(A,B,C,D)

33.(A,B,C) **34.**(A,B,C) **35.**(B,D) **36.**(A,C,D) **37.**(A,D) **38.**(B) **39.**(B)

40.(B)

Exercise-III

1.(i) I_2 + NaOH (ii) WKR (iii) Zn/Hg-HCl (iv) not $LiAH_4$ (v) N_2H_2

2.(a) $NaBH_4$ (b) $NaBH_4$ (c) Na + C_2H_5OH (d) $LiAlH_4$ (e) H_2–Pd/$BaSO_4$ (f) $NaBH_4$ (g) N_2H_2

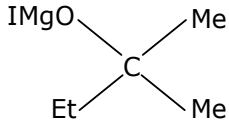
3. In acidic medium $Me_2\overset{OCH_3}{\overset{|}{C}}-\underset{OH}{\overset{|}{CH_2}}$ and in basic medium $Me_2\overset{OCH_3}{\overset{|}{C}}-\underset{O^{\ominus}}{\overset{|}{CH_2}}$

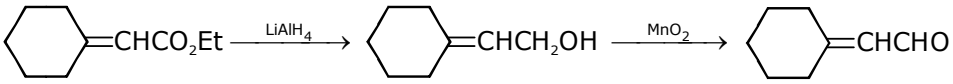
4. (a) 1-hexanol reduces organ red CrO_3 to green Cr^{3+}; while 1-chlorohexane gives white ppt. of AgCl on warming with ethanolic $AgNO_3$.
(b) n-Butanol gives a positive test with CrO_3 in acid and evolves H_2 with sodium; while dry ethyl ether is negative to both tests.
(c) Unlike n-pentane, diethyl ether is basic and dissolves in conc. H_2SO_4.
$(C_2H_5)_2O + H_2SO_4 \longrightarrow (C_2H_5)_2OH^+ + HSO_4^-$

5. (i) MeI + EtOH due to S_N2 mechanism (ii) No reaction

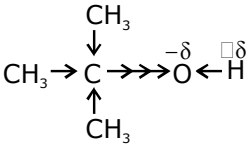
8. (i) $n\text{-}C_3H_7CO_2H \xrightarrow[\text{or } B_2H_6]{LiAlH_4} n\text{–}H_9OH$

(ii) $Me_2CO + EtMgI \longrightarrow M_2C\begin{matrix}\diagup OMgI \\ \diagdown Et\end{matrix} \xrightarrow{H^+} Me_2C(OH)\,Et$

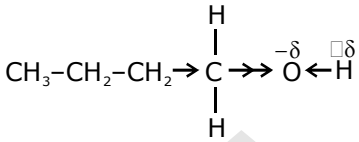
(iii) $EtCO_2Et + 2MeMgI \longrightarrow$  $\xrightarrow{H_2O} EtCMe_2OH$

(iv) 

7. The +I.E. of three methyl groups on ce ntral C-atom of tert-butyl alcohol makes is partially negative with the result that it pushes the electron pair of –OH bond towards H-atom and thus H-atom is not replaced easily.



(less partial + ve charge)



(more partial +ve charge)

8. Oxygen atom is diethyl ether molecule has two ione pair of electron available for co-ordination. Therefore ether behave as Lewis base forming oxonium salts.

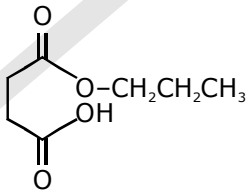
$\begin{matrix}R\diagdown \\ \\ R\diagup\end{matrix}O + HCl \longrightarrow R_2IO^+Cl^-$ (dialkyl oxonium chloride)

9. Due to formation of explosive peroxide by oxidation.

10. Ethanol being very weak Lewis base and thus reacts with stronger acid HI

11. (i) CH_3CH_2COOH (ii) $CH_3COOCH_2CH_2CH_3$ (iii) $MePhSO_2OCH_2CH_2CH_3$

(iv) $PhCOOH + PhCOOCH_2CH_2CH_3$

(v) 

12. A → P; B → Q,R; C → S **2.** X → (ii), Y → (i), (iv), (v), Z → (iii)

13. A → (ii), Y → (i), (iv), (v), Z → (iii)

14. A → P, S; B → P, S; C → P, S; D → P, S, E → R

15. A → P; B → Q; C → R; D → S

16. A → Q, r, S ; B → R, S; C → Q ; D → P

17. A → R; B → R, S ; C → P, R, T ; D → Q

18. A → P, Q, R; B → P, Q, R; C → P, Q, R; D → S

19. A → P, Q, R; B → P, Q, R; C → P, Q, R; D → S

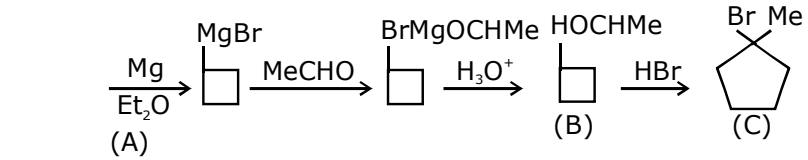
Exercise-IV (LEVEL-I)

1. B **2.** D **3.** C **4.** D **5.** D **6.** C **7.** C **8.** C **9.** B **10.** B

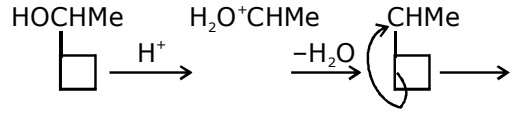
Exercise-IV (LEVEL-II)

1. (C) **2.** (B) **3.** (A) **4.** (D) **5.** (B) **6.** (C) **7.** (D)

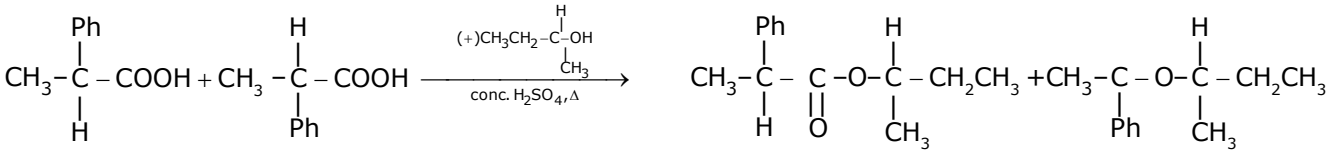
8.



Mechanism

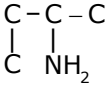


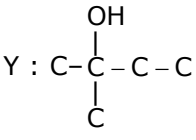
2ºcarbonium 3ºcarbonium

9. 

(recemic mixture)

during esterification reaction only–COOH and –OH participates. Tehre is no effect on structure of configuration of catrbon adjacent of these group. So when (±) acid reacts with pure (+) alcohol two esters are produced whinc are diastereoisomers of each other.

10. X : 

Y : 

11. A → Q, S, T ; B → S, T; C → P., D → R

Y is optically inactive.